

The Photolysis of 2-Phenyltetrazole

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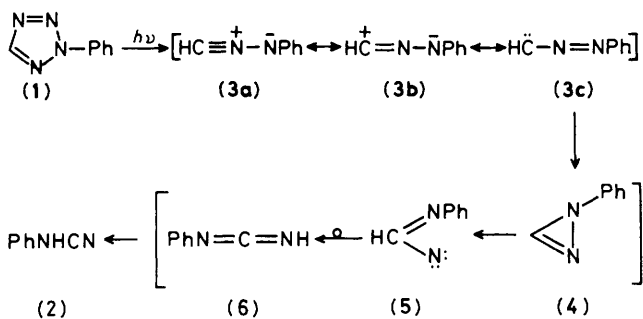
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The photolysis of 2-phenyltetrazole (**1**) in benzene yields phenylcyanamide (27%) and the phenylhydrazone of *o*-aminobenzoyl cyanide (53%) whose structure was determined by *X*-ray crystal structure analysis.

We have investigated the photolysis of 2-phenyltetrazole (**1**)¹ and now describe our results. Photolysis of (**1**) in benzene using a low pressure mercury lamp (Ricoh Kagaku Sangyo Co.

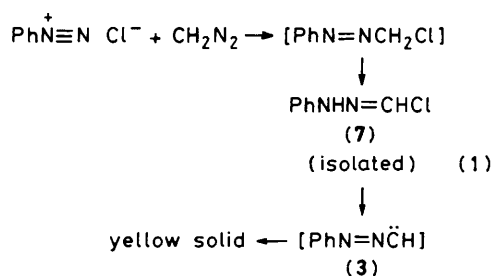
UVL300 Q) under nitrogen for 15 h gave (**2**) in 27% yield and an unknown canary-yellow compound (53%), m.p. 155—157 °C. The appearance of a parent peak at 236 in the mass



spectrum of the unknown solid established its molecular formula as $C_{14}H_{12}N_4$. The high resolution (300 MHz) 1H n.m.r. spectrum in deuteriochloroform displayed two active hydrogen signals at δ 5.67 (2H) and 8.62 (1H); analysis of the aromatic multiplet centered at δ 7.18 indicated the presence of a mono-substituted phenyl ring and an *ortho*-disubstituted aromatic ring. The most intriguing spectral property of the unknown product was a sharp nitrile peak at 2252 cm^{-1} in the i.r. spectrum.

The formation of phenylcyanamide (2), and presumably of the unknown product, can only be rationalized *via* the intermediacy of the 1*H*-diazirine (4). Fischer and Wentrup² have recently suggested that the ring-opening of such 1*H*-diazirines which in the present case could have arisen from the azocarbene intermediate (3),³ can account for the formation of carbodi-imides (6) (Scheme 1).

Huisgen and Koch⁴ isolated a compound corresponding to the $C_{14}H_{12}N_4$ formula with a similar melting point (151–151.5 °C) from the reaction of benzenediazonium chloride with diazomethane in methanol containing lithium chloride and lithium carbonate (equation 1). The i.r. spectrum reported⁴



displayed a nitrile peak at 2252 cm^{-1} ; the structure of this compound was not established. However, they were able to isolate the chloride (7) which could, in principle, lead to the same intermediate nitrilimine \rightleftharpoons azocarbene by the loss of the elements of hydrogen chloride; this possibility was particularly attractive since these investigators obtained their unknown product in the *presence* of calcium carbonate. Repetition of the reported procedure⁴ gave a product which was completely identical to our unknown. The X-ray crystal structure of the unknown was determined; suitable crystals were obtained from hexane.

Crystal data: $C_{14}H_{12}N_4$, $M = 236.28$, monoclinic, $a = 13.646(1)$, $b = 5.394(1)$, $c = 19.307(3)$ Å, $\beta = 212.57(1)^\circ$, measured from preliminary diffraction experiments; 1830 reflections were measured with Cu- K_α radiation and 1265 were observed [$I > 3\sigma(I)$]. Systematic absences indicated the space group $P2_1/c$ with $Z = 4$. The structure was solved with direct

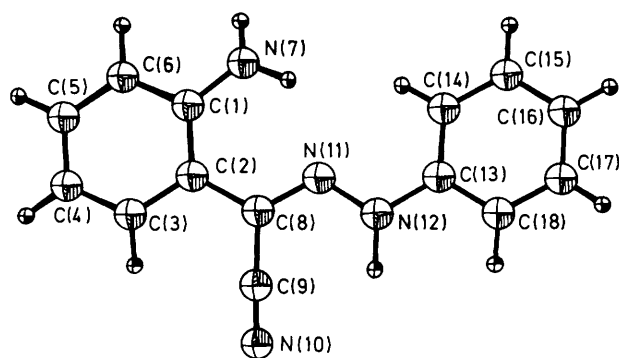
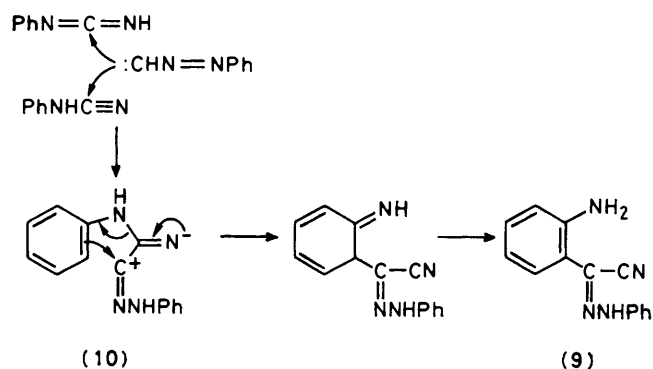
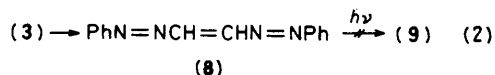


Figure 1



methods⁵ and refined using full-matrix least-squares techniques⁶ by minimizing $\sum \omega (|F_o| - |F_c|)^2$ with $\omega = 1/(\sigma F_o)^2$. The final unweighted R factor was 0.041. Figure 1 is a computer drawing of the molecule (9).⁷ The molecule is essentially planar with no abnormal bond distances or angles.[†]

The totally unexpected structure of the product (9) as the phenylhydrazone of *o*-aminobenzoyl cyanide requires considerable reorganization of the skeleton of the putative azocarbene intermediate (3). The most striking requirement is that a carbon-carbon bond be formed from the two azocarbenes. While some suggestions have been presented regarding the 'dimerization' of isonitriles,^{3d,8} the fact that the dimer 1,2-bis(phenylazo)ethylene (8)⁹ is stable under the conditions of the photolysis eliminates it as a possible precursor of (9) (equation 2). A more plausible rationalization would involve



nucleophilic attack of the azocarbene (3) on its rearrangement products, either the carbodi-imide (6) or phenylcyanamide (2) to yield (10) as shown in Scheme 2. Cyclization to an indole-type structure followed by ring opening or concerted reorganization of (10) would lead to the observed product after appropriate hydrogen shifts. It is interesting to note that while phenylcyanamide was formed from the photolysis of 1-phenyl-

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

tetrazole, no product corresponding to (9) was observed. This result suggests that while (3) can apparently be converted into (5), the reverse process does not occur.

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