

PHOTOCHEMICAL TRANSFORMATION OF TROPONE PHENYLHYDRAZONE  
TO 2-PHENYLINDAZOL

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We wish to report a novel photochemical transformation of tropone phenylhydrazone (I) to 2-phenylindazole (II) and a related chemical reaction of I with lead tetraacetate. The photochemical formation of II from I is the first example not only in troponoid chemistry, but also in photochemistry of hydrazones.

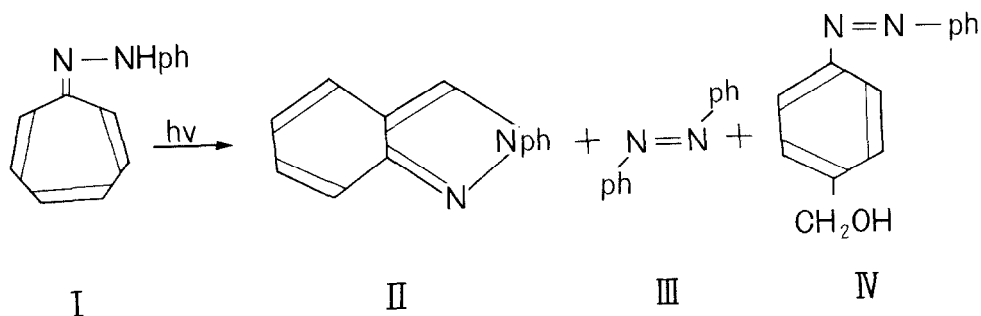
A benzene solution of I (1) ( $10^{-2}$  M) was irradiated with a high pressure mercury lamp through Pyrex filter under nitrogen atmosphere. The reaction was followed by disappearance of an absorption at 355 m $\mu$ , that is the longest absorption maximum of I. The absorption of I disappeared completely after irradiation for 5 days, and several products were obtained. Alumina chromatographic purification of the reaction mixture afforded four compounds: m.p. 81° (II), m.p. 68° (III), m.p. 137° (IV) and an oil (V) in 13, 7, 2 and 2% yields respectively, accompanied with a large amount of polymeric materials.

The structures of II, III and IV were deduced on the basis of the following physical properties, and finally confirmed to be 2-phenylindazol (2) trans azobenzene and p-hydroxymethylazobenzene (3) respectively by comparison with authentic samples prepared by methods described in the literature (2,3).

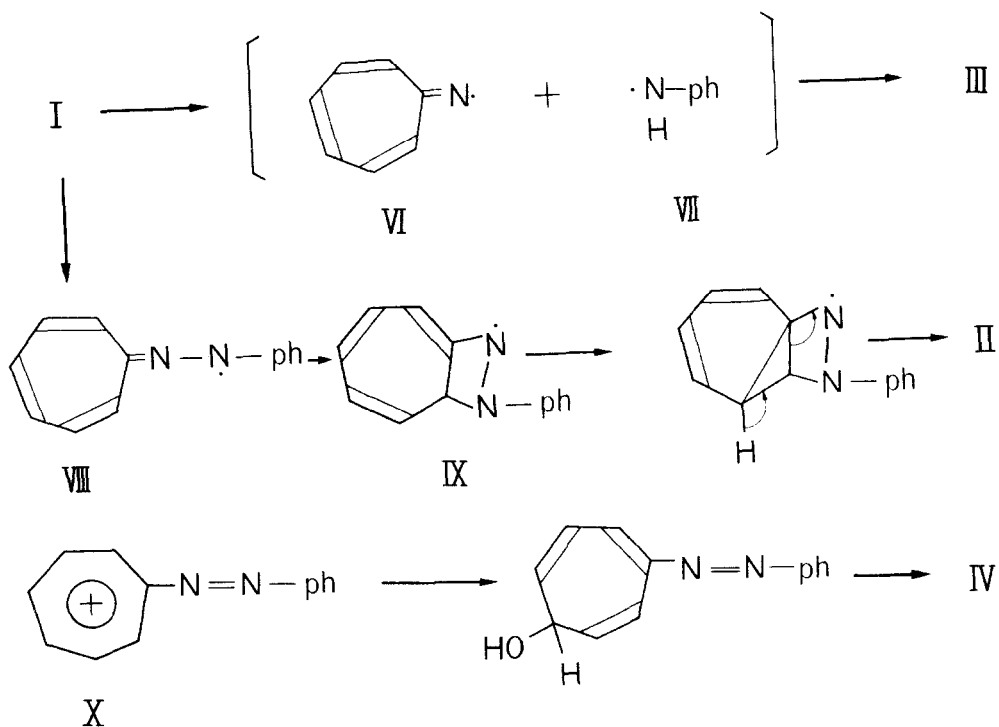
Compound II, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub> (4): mass spectrum (m/e), 194 (M<sup>+</sup> and base ion), 166 and 77; ultraviolet spectrum (5)  $\lambda_{\max}^{\text{MeOH}}$  (log  $\epsilon$ ), 297 (4.19) and 273 (4.32) m $\mu$ ; infrared spectrum (KBr), 3145, 3058, 1626, 1590, 754 and 685 cm<sup>-1</sup>; nmr spectrum (60 Mc in CCl<sub>4</sub>), 8.36 (1H, singlet) and 7.5 (4H, multiplet) ppm. Compound IV, C<sub>13</sub>H<sub>12</sub>N<sub>2</sub>O; mass spectrum (m/e), 212 (M<sup>+</sup>) 135, 107 and 77 (base ion); ultraviolet spectrum (6)  $\lambda_{\max}^{\text{MeOH}}$  (log  $\epsilon$ ), 440 (3.16), 322 (4.39) and 232 (4.33) m $\mu$ ; infrared spectrum (KBr) 3344, 3279, 1020, 848, 829, 769 and 684 cm<sup>-1</sup>; nmr spectrum

(in  $\text{CDCl}_3$ ), 7.7 (9H, multiplet), 4.75 (2H, singlet) and 1.60 (1H, broad singlet, replaceable by deuterium) ppm.

The structure of V was not elucidated but is thought to be a 1-substituted cycloheptatriene derivative (7) on the basis of its nmr spectrum (8).



The formation of II, III and IV may be interpreted by the following scheme.



A process of the photochemical dissociation of the N-N bond of I to radicals VI and VII is supported by analogous examples in aromatic aldazines (9) and benzaldehyde phenylhydrazone (10). In addition photolysis of highly diluted benzene solution of I ( $10^{-5}$  M), tropone azine (11, 12) or tropone oxime (1,12) resulted in the formation of a species which has absorption maxima at 358 ( $\log \epsilon$ : 4.31), 378 (4.35) and 400 (4.35)  $\mu$ . This species may arise from the radical VI, which is generated by the cleavage of the N-N or N-O bond of the photolyzates (13), and assumed to be a derivative of N,N'-disubstituted-1-amino-7-imino-1,3,5-cycloheptatriene by comparison of ultraviolet spectrum with 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (14).

The proposition that the radical (VIII) is formed from I by hydrogen abstraction and that VIII transforms to 2-phenylindazol (II) via an intermediate (IX) is supported by the fact that lead tetraacetate oxidation of I afforded II in 20% yield accompanied with 5% of III. The ready formation of similar types of azaradicals has been reported in the oxidation of phenylhydrazones with lead tetraacetate (15) as well as with other oxidizing reagents (16), suggesting the assumed radical intermediate.

A possible hydrogen acceptor in the formation of VIII from I is the radical VI; tropone imine (11) so formed is assumed to be too unstable to exist under photolytic condition. Alternatively, oxygen contaminated in the nitrogen gas may be able to act as the hydrogen acceptor (17). Though it is not decisive we prefer the former possibility in this case, because no oxygenated products such as tropone (17) was found in the reaction mixture. It is to be noted that the addition of benzophenone (10 mole eq.) to the photolyzate solution of I resulted in an increase of the yield of II to 30%.

Azobenzene (III) is probably formed from VII by coupling and subsequent dehydrogenation or by coupling of phenylnitrene which is generated from VII by loss of a hydrogen, or alternatively from VIII.

The other minor product (IV) may be formed via phenylazotropylium ion (X), which probably arises from (or its isomer) by the hydrogen abstraction, or from VIII by electron transfer.

## REFERENCES AND FOOTNOTES

1. T. Nozoe, T. Mukai and K. Takase, Sci. Repts. Tohoku Univ. Ser. I, 39, 164 (1956); T. Mukai, Bull. Chem. Soc. Japan, 33, 238 (1960).
2. J.I.G. Cadogan, M. Cameron and R.K. Mackie and R.J.G. Seattle, J. Chem. Soc., 1965, 4831.
3. H. Nanya, J. Chem. Soc. Japan (Nippon Kagaku Zasshi) Pure Chem. Sect. 80 219 (1959).
4. Satisfactory elemental analyses were obtained for II, III and IV.
5. O. Dann and P. Nickel, Ann., 667, 101 (1963).
6. R. Schroyzer, P. Sieber and K. Zatsko, Helv. Chim. Acta, 41, 491 (1958).
7. C.W. Borden, O.L. Chapman, R. Swindel and T. Tezuka, J. Am. Chem. Soc., 89, 2879 (1967); T. Tezuka, M. Kimura, A. Sato and T. Mukai, Bull. Chem. Soc. Japan, submitted.
8. The nmr spectrum of V showed signals at 3.06 (2H; doublet,  $J=7.2$  cps), 5.50 (1H; multiplet), 6.28 (1H; multiplet), 6.72 (2H; multiplet), 7.12 (1H; multiplet) and of phenyl group around 7.7 ppm.
9. J.E. Hodgkins and J.A. King J. Am. Chem. Soc., 85, 2679 (1963); R.W. Binkley, J. Org. Chem., 33, 2311 (1968).
10. On a way of this studies we found a publication concerning the photochemistry of benzaldehyde phenylhydrazone; see R.W. Binkely, Tetrahedron Letters, 1969, 1893.
11. M. Funamizu, PhD thesis, Tohoku University, 1966.
12. When a concentrated benzene solution of tropone azine or oxime ( $10^{-2}$  M) was irradiated, the starting material was recovered almost quantitatively.
13. T. Okada, M. Kawanishi and H. Nozaki, Bull. Chem. Soc. Japa, 42, 2981 (1969).
14. W.R. Brasen, H.E. Holmquist and R.E. Benson, J. Am. Chem. Soc. 83, 3125 (1961).
15. D.C. Iffland, L. Salisbury and W.R. Schafer, ibid., 83, 747 (1961).
16. (a) K.H. Pausacher, J. Chem. Soc., 1950, 3478; R. Criegee and C. Lokous, Chem. Ber., 84, 219 (1951). (b) L. Bhautnagar and M.V. George, J. Org. Chem., 32 2252 (1967). (c) A.T. Bellamy and R.D. Guthrie, J. Chem. Soc., 1965, 3258.
17. Irradiation of benzene solution of benzaldehyde or dibenzylketone phenylhydrazone ( $10^{-2}$  M) in the presence of oxygen afforded benzaldehyde or dibenzyl ketone, respectively (T. Tezuka, H. Sukawa, A. Yanagi and T. Mukai, to be published).