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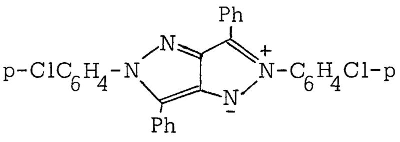
OXIDATION OF 2,5-BIS(p-CHLOROPHENYL)-3,6-DIPHENYL-1,2,4,5-TETRAAZAPENTALENE AND SOME PROPERTIES OF THE PRODUCTS

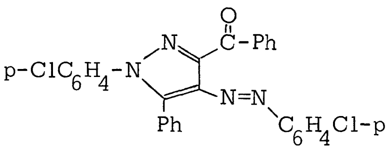
Akira MATSUMOTO, Joung Hee LEE, Masayuki YOSHIDA, and Osamu SIMAMURA
Department of Chemistry, Faculty of Science, Tokyo University, Hongo, Tokyo

The title compound (I) was oxidized to give 3-benzoyl-1-p-chlorophenyl-4-p-chlorophenylazo-5-phenylpyrazole (II) and 3-benzoyl-1-p-chlorophenyl-4-p-chlorophenylazoxy-5-phenylpyrazole (III), both of which underwent trans to cis isomerization on irradiation with ultraviolet light.

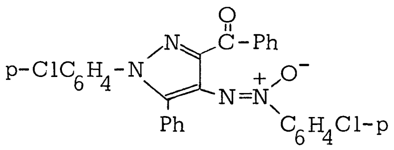
Oxidation of 2,5-bis(p-chlorophenyl)-3,6-diphenyl-1,2,4,5-tetraazapentalene[1] (I) with potassium permanganate in a mixture of pyridine and water (3 : 1) at 90° gave a crystalline compound (yellow needles, 64%), $C_{28}H_{18}Cl_2N_4O$, mp 207-208° (decomp.), λ_{max} (EtOH) 244 (log ε 4.65) and 344 (4.33) nm, $\nu_{C=O}$ (KBr) 1665 cm^{-1}, M^+ 496. Evidently this is 3-benzoyl-1-p-chlorophenyl-4-p-chlorophenylazo-5-phenylpyrazole (II), and the structure is further supported by the presence of a peak at m/e 105 ($PhCO^+$) in its mass spectrum and the formation of the 2,4-dinitrophenylhydrazone, mp 235° (decomp.). Catalytic hydrogenation in acetic acid with 10% Pd/C gave 4-amino-3-benzoyl-1-p-chlorophenyl-5-phenylpyrazole as yellow needles (16%), $C_{22}H_{16}ClN_3O$, mp, 182°, ν_{max} (KBr) 3460 and 3370 (NH_2) and 1625 (C=O) cm^{-1}.



(I)



(II)



(III)

Oxidation of the tetraazapentalene (I) with peroxybenzoic acid in dichloromethane gave pale yellow needles (III, 13%), $C_{28}H_{18}Cl_2N_4O_2$, mp 179-180° (decomp.), λ_{max} (EtOH) 261 (log ε 4.47) and 355 (4.03) nm, $\nu_{C=O}$ (KBr) 1640 cm^{-1}, M^+ 512, and greenish yellow plates (IV, 16%), mp 175-179° (decomp.). Compound III is assigned the structure of 3-benzoyl-1-p-chlorophenyl-4-p-chlorophenylazoxy-5-phenylpyrazole on the basis of the above spectral data and of its mass spectrum with a fragmentation pattern very similar to that of compound II and a peak at m/e 496 (M^+ - 16, 16%). Further it was formed from compound II by the action of m-chloroperoxybenzoic acid in acetic acid at 60° and deoxygenated to compound II by heating with triethyl phosphite at 155°.[2)]

The substance crystallizing in greenish yellow plates (IV) was shown to consist of compounds II and III in approximately equal amounts, by means of thin layer chromatography on silica-gel in benzene and by inspection of its spectra (IR (KBr), UV (EtOH) and Mass), and thus seems to be a 1 : 1 molecular compound of II and III. This is supported by the fact that it was always formed by condensing alcoholic solutions of II and III in any relative amounts.

An alcoholic solution of compound II was condensed in vacuo at 20° under irradiation with ultraviolet light (365 nm) to yield orange crystals (IIc), $C_{28}H_{18}Cl_2N_4O$, mp ca. 150°, λ_{max} (EtOH) 257 (log ε 4.73) and 435 (3.49) nm, and the mass spectrum was almost the same as that of II. The compound (IIc) reverted to II when heated in alcohol for about half an hour. The ultraviolet spectra of II and IIc are quite similar in appearance to those of trans- and cis-azobenzene,[3)] respectively. These findings establish the structures of II and IIc as trans- and cis-3-benzoyl-1-p-chlorophenyl-4-p-chlorophenylazo-5-phenylpyrazole.

Similarly, the azoxy-compound (III) was photo-isomerized to yellow crystals (IIIc), mp ca. 120° (decomp.), λ_{max} (EtOH) 260 (log ε 4.60) and 355 (3.58) nm, and the mass spectrum was very similar to that of III. This compound (IIIc) also reisomerized to the initial compound (III) in hot alcohol. The assignment of trans- and cis-azoxy configurations to III and IIIc, respectively, was evident from comparison of the ultraviolet absorption spectra with those of trans- and cis-azoxybenzene.[3)] Although the position of the azoxy-oxygen in III and IIIc is uncertain at present, it is reasonable to prefer the less crowded 4-p-chlorophenyl-ONN-azoxy structure.[4)]

It is noteworthy that compound II and triethyl phosphite, heated under reflux for 21 hours under nitrogen, gave the initial tetraazapentalene (I) in a yield of 68%; the reaction suggests the intermediacy of a carbene which may be formed by deoxygenation with the phosphite.[5)]

References

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