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NEW ROUTES TO 1,2-DIAZOLES WITH A FUSED RING SYSTEM BY REDUCTIVE AND OXIDATIVE CYCLIZATIONS

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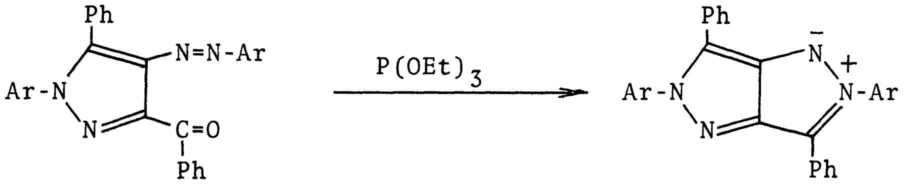
Heating aromatic or heteroaromatic compounds carrying a carbonyl and an arylazo group at adjacent nuclear positions with triethyl phosphite resulted in the formation of a 1,2-diazole ring through reductive cyclizations. Similar, but oxidative, cyclizations were effected by the action of selenium dioxide on compounds with a methylene group at an appropriate position.

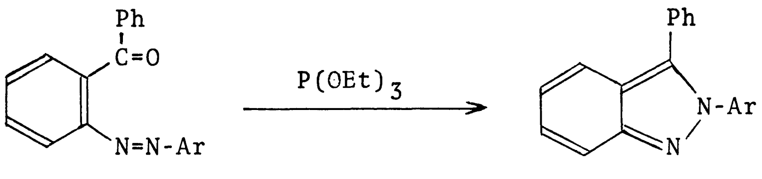
We have found that 3-benzoyl-1-p-chlorophenyl-4-p-chlorophenylazo-5-phenylpyrazole (Ia), on prolonged heating in boiling triethyl phosphite, deposits 2,5-bis-(p-chlorophenyl)-3,6-diphenyl-1,2,4,5-tetra-azapentalene (IIa, 68%).[1] Similarly, benzoylpyrazoles, Ib[2] (mp 205-206°C) and Ic (mp 170.5-171°C), afforded the corresponding tetra-azapentalenes, IIb[2] (82%) and IIc (96%), $C_{28}H_{20}N_4$, mp 315°C, λ_{max} ($CHCl_3$) 281 and 394 nm (log ε = 4.34 and 4.33, respectively).



Ia: Ar = p-ClC_6H_4
b: Ar = p-BrC_6H_4
c: Ar = C_6H_5

II

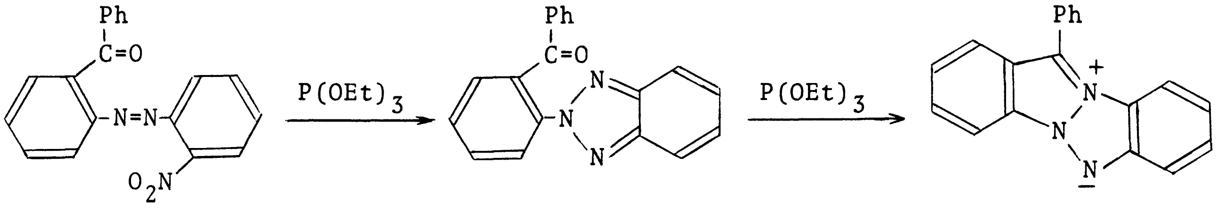
2-Phenylazobenzophenone (IIIa), mp 49°C, obtained by condensation of 2-aminobenzophenone[3] with nitrosobenzene in glacial acetic acid, was reductively cyclized in a similar way to 2,3-diphenylindazole (IVa, 58%), $C_{19}H_{14}N_2$, mp 109.5-110°C, λ_{max} (EtOH) 301 and 312 (shoulder) nm (log ε = 4.13 and 4.12, respectively). 2-p-Chlorophenylazobenzophenone (IIIb), mp 86-86.5°C, gave 2-p-chlorophenyl-3-phenylindazole (IVb, 87%), $C_{19}H_{13}ClN_2$, mp 126°C, λ_{max} (EtOH) 300 nm (log ε = 4.15).



IIIa: Ar = C_6H_5
b: Ar = p-ClC_6H_4

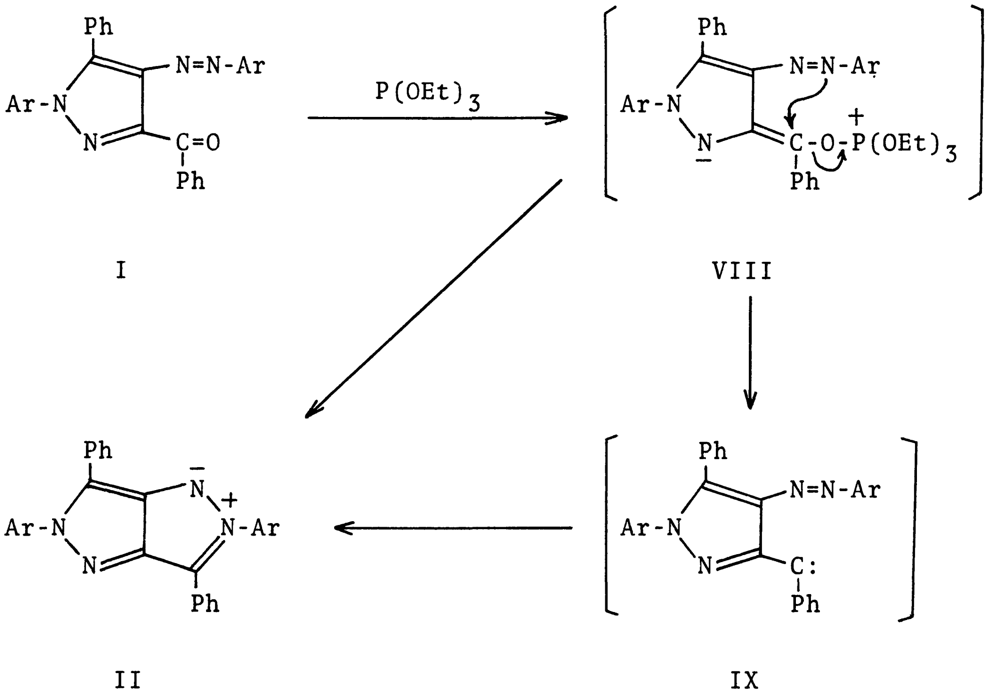
IV

A related reaction is the reductive cyclization of 2-o-nitrophenylazobenzophenone (V) to 11-phenylindazolo[2,1-a]benzotriazole (VII). Condensation of 2-aminobenzophenone with o-nitronitrosobenzene[4] in glacial acetic acid yielded 2-o-nitrophenylazobenzophenone (V, 54%), $C_{19}H_{13}N_3O_3$, mp 99-99.5°C. Reduction of this compound (V) with triethyl phosphite at 160-170°C afforded 2-(o-benzoylphenyl)-2H-benzotriazole (VI, 55%), $C_{19}H_{13}N_3O$, mp 143-144°C, the structure being confirmed on the basis of its ir spectrum [$\nu_{C=O}$ 1660 cm^{-1} and the disappearance of the absorption due to a nitro group in the starting material (ν_{NO_2} 1520 and 1360 cm^{-1})] and analytical data. On heating in triethyl phosphite at 180-200°C, the triazole (VI) gave the tri-azapentalene (VII, 57%), $C_{19}H_{13}N_3$, mp 219-200°C, λ_{max} ($CHCl_3$) 280, 460 (shoulder), and 481 nm (log ε = 4.51, 4.01, and 4.12, respectively).



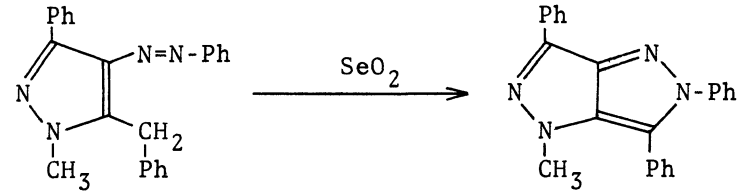
V VI VII

The mechanism of the present reaction is not certain. However, the cyclization of the benzoylazopyrazole (I) with triethyl phosphite may be formulated as follows:

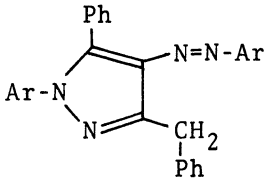


It seems probable that an oxyphosphonium betaine (VIII) intervenes, a nitrogen lone pair on the azo group displacing the C-O bond to afford the final product (II). The result can also be rationalized by assuming the intermediacy of a carbene (IX), which may be formed by loss of triethyl phosphate from VIII. Evidence in support of such intermediates is found in the reaction of fluorenone with tervalent phosphorus reagents.[5] Nomura and his co-workers also indicated the intermediacy of a vinyl carbene in the reaction of trans-dibenzoylethylene with triphenylphosphine in the presence of N-phenylmaleimide.[6]

The possibility of an analogous, but oxidative, cyclization starting from compounds with a methylene group instead of a carbonyl group was realized by using selenium dioxide as an oxidizing reagent. Thus, although a methylene group activated by two aryl groups is known to be easily converted into a carbonyl group with selenium dioxide,[7] treatment of 5-benzyl-1-methyl-3-phenyl-4-phenylazopyrazole[8] (X) with selenium dioxide in acetic acid at 80-90°C afforded 1-methyl-3,5,6-triphenyl-1,2,4,5-tetra-azapentalene[8] (XI, 83%). 3-Benzyl-1-p-chlorophenyl-4-p-chlorophenylazo-5-phenylpyrazole[2] (XIIa) and 3-benzyl-1,5-diphenyl-4-phenylazopyrazole[9] (XIIc) were similarly cyclized by the selenium dioxide oxidation to the tetra-azapentalenes, IIa (14%) and IIc (12%), respectively.



X XI



XIIa: Ar = p-ClC_6H_4
c: Ar = C_6H_5

Satisfactory elemental analysis and supporting spectral data have been obtained for all compounds reported.

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