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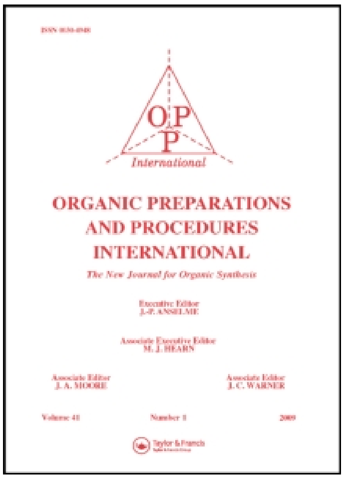

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ORGANIC PREPARATIONS AND PROCEDURES INT. 6(4), 161-167 (1974)

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THE FORMATION OF 1H-DIBENZO[b,g][1,4,5]TRIAZAPENTALENE FROM 2-(o-NITROPHENYL)- AND 2-(o-AZIDOPHENYL)-2H-INDAZOLE

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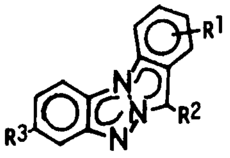
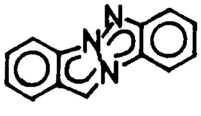
The preparation of new aromatic azapentalenes, dibenzo[b,e][1,3a,6a]-triazapentalenes (I), by the reductive cyclization of 1-(o-nitrophenyl)-1H-indazoles with triethyl phosphite and by the thermolysis or photolysis of 1-(o-azidophenyl)-1H-indazoles has been recently reported.[1,2] Since I exhibited very interesting chemical behaviour towards electrophiles[3] and acetylenes,[4,5] we attempted to prepare an isomer of Ia ($R^1 = R^2 = R^3 = H$), dibenzo[b,f][1,3a,6a]triazapentalene (II), from 2-(o-nitrophenyl)-2H-indazole or 2-(o-azidophenyl)-2H-indazole, in order to investigate the difference of reactivity between I and II.



I

R^1, R^2, R^3:
H, Me, or Cl



II

However, the arylation of indazoles with o-chloronitrobenzenes gave only the corresponding 1-aryl-1H-indazoles and none of 2-aryl isomers.[1,2] Therefore, 2-(o-nitrophenyl)-2H-indazole (IV), a possible precursor of II, had to be prepared by a method other than the direct arylation of indazole.

We applied the reaction of 3-(o-nitrophenyl)sydnone (III) with benzyne to the preparation of IV. As expected, the reaction of III[6] (obtained from

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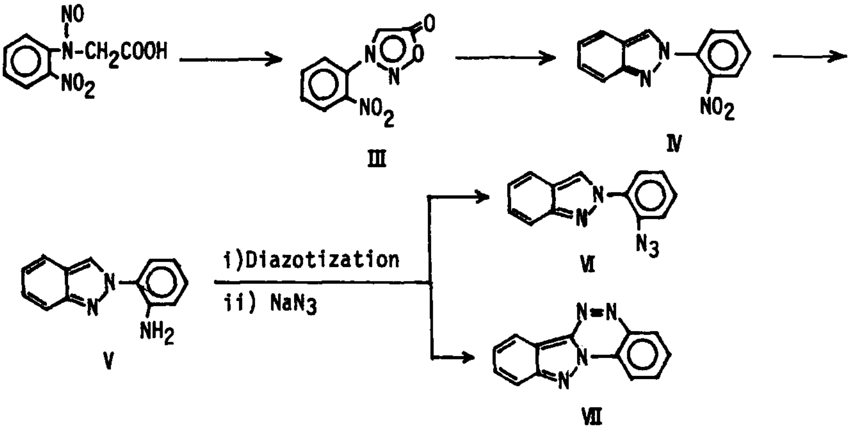
N-nitroso-N-(o-nitrophenyl)glycine) with benzyne (generated from anthranilic acid and iso-amyl nitrite) in refluxing tetrahydrofuran afforded IV in 43% yield. Another possible precursor, 2-(o-azidophenyl)-2H-indazole (VI), was prepared from the diazotization of 2-(o-aminophenyl)-2H-indazole (V) obtained by the reduction of IV, followed by the treatment with sodium azide. In this reaction VI was obtained in 63% yield, together with 12% yield of dibenzo[b,g]pyrazolo[3,2-c][1,2,4]triazine (VII). The formation of VII might be viewed as arising from intramolecular diazo coupling reaction of diazonium salt. The structures of IV-VII were confirmed on the basis of their spectral data as well as of the microanalyses.



Scheme 1

When a solution of IV and triethyl phosphite in xylene was refluxed for 10 hr under a stream of nitrogen, a product VIII, mp 289-291° (dec.), whose molecular formula agreed with that of the expected triazapentalene II, was obtained in 29% yield. However, its IR spectrum showed the characteristic absorption band ascribable to the NH group of a pyrazole or of an imidazole ring at 2700-3100 cm^{-1} and its UV spectrum was considerably different from that of Ia. On the basis of the above observations and of the mode of formation, VIII was assumed to be 1H-dibenzo[b,g][1,4,5]triazapentalene or its

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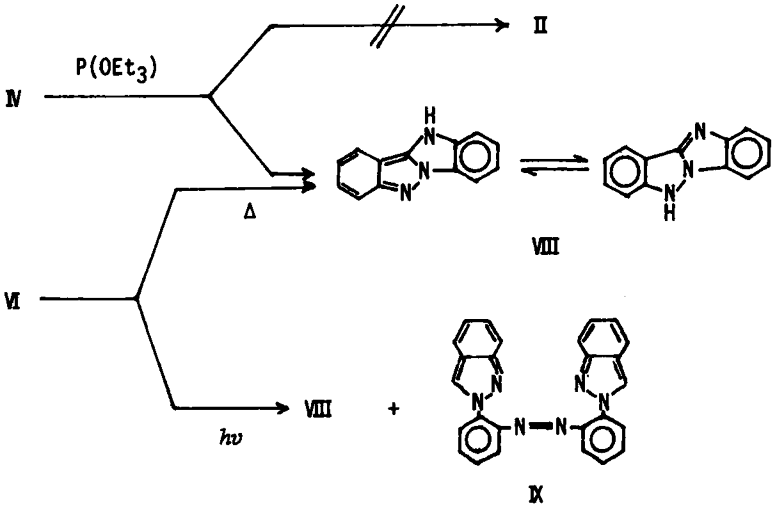
tautomer (Scheme 2).

The thermal decomposition of VI in xylene under reflux for 3.5 hr afforded VIII in 76% yield. On the other hand, when a benzene solution of VI was irradiated by a 100W high-pressure mercury lamp with a Pyrex filter at room temperature, VIII was formed in 63% yield, together with trace amounts of IX of red prisms, mp 144-145°, Similar irradiation in the presence of acetophenone as a sensitizer afforded VIII and IX in 11% and 46% yields respectively. The product IX was shown to be 2,2'-di(2-indazolyl)azobenzene on the basis of the analytical and spectral data as well as by the unequivocal synthesis from IV.



Scheme 2

Experimental

All the melting points are uncorrected. The NMR spectra were determined at 60 MHz with a Hitachi R-20 NMR spectrometer using TMS as an internal reference. The mass spectra were obtained on a Hitachi RMS S-4 mass spectrometer using a direct inlet and an ionization energy at 70 eV. The

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IR spectra were measured as KBr pellets.

2-(o-Nitrophenyl)-2H-indazole (IV).— To a gently refluxing solution of 1.7 g (7.2 mmol) of 3-(o-nitrophenyl)sydnone (III),[6] 0.98 g (7.2 mmol) of anthranilic acid and 20 mg of trichloroacetic acid in 20 ml of dry tetrahydrofuran, 2 ml of iso-amyl nitrite was added dropwise and the reaction mixture was refluxed for an additional hour after addition of nitrite. The solvent was removed in vacuo to leave a residue which was chromatographed on silica gel using benzene as an eluent to give yellow crystals; recrystallization from benzene afforded 0.85 g (43%) of IV, mp 163-163.5°, as yellow prisms.

Anal. Calcd for $C_{13}H_9N_3O_2$: C, 65.29; H, 3.79; N, 17.57.

Found: C, 65.46; H, 3.55; N, 17.68.

Mass spectrum m/e: 239 (M^+).

NMR ($CDCl_3$) δ: 6.9-8.0 (8H, m, aromatic protons), 8.14 (1H, s, CH).

2-(o-Aminophenyl)-2H-indazole (V).— To a vigorously stirred suspension of 2.0 g of IV and 16 g of iron powder in 100 ml of ethanol, an ethanolic hydrochloric acid (5 ml of conc. HCl and 40 ml of EtOH) solution was added dropwise under reflux over a period of 2 hr. The reaction mixture was refluxed for an additional hour and filtered. The filtrate was made slightly basic (pH about 8) with aqueous potassium hydroxide solution and filtered again. Evaporation of the filtrate in vacuo gave crystals, which on recrystallization from water gave 1.6 g (92%) of V, mp 135-136°, as colorless needles.

Anal. Calcd for $C_{13}H_{11}N_3$: C, 66.37; H, 3.86; N, 29.77.

Found: C, 66.35; H, 3.88; N, 29.82.

IR (KBr) cm^{-1}: 3460, 3380 (νNH).

Mass spectrum m/e: 209 (M^+).

2-(o-Azidophenyl)-2H-indazole (VI).— A solution of 1.3 g of sodium nitrite in 10 ml of water was added dropwise to a stirred solution of 2.8 g of V in

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10 ml of 5N hydrochloric acid at 0° over a period of 1 hr, and stirring was continued for an additional hour after the nitrite addition. A solution of 1.8 g of sodium azide in 10 ml of water was slowly added to the diazonium solution at 5° with continued stirring during which time nitrogen was evolved. The mixture was stirred for an additional 2 hr and the precipitated crystals were filtered. Fractional recrystallization from methanol gave 2.0 g (63.5%) of VI and 0.36 g (12%) of dibenzo[b,g]pyrazolo[3,2-c][1,2,4]-triazine (VII).

VI: mp 149-150° (dec.), yellow prisms.

Anal. Calcd for $C_{13}H_9N_5$: C, 66.37; H, 3.86; N, 29.77.

Found: C, 66.42; H, 3.93; N, 29.67.

IR (KBr) cm^{-1}: 2170 (νN_3).

Mass spectrum m/e: 235 (M^+).

VII: mp 195-196°, yellow needles.

Anal. Calcd for $C_{13}H_8N_4$: C, 70.89; H, 3.66; N, 25.44.

Found: C, 70.73; H, 3.39; N, 25.48.

Mass spectrum m/e: 220 (M^+).

Reaction of IV with Triethyl Phosphite.—After a solution of 0.53 g (2.2 mmol) of IV and 1.2 g (7.2 mmol) of triethyl phosphite in 10 ml of xylene had been refluxed for 10 hr under a stream of nitrogen, the reaction was evaporated *in vacuo* to leave a residue. The residue was chromatographed on silica gel using benzene as an eluent to give colorless crystals, which on recrystallization from benzene afforded 0.13 g (28%) of 1H-dibenzo[b,g]-[1,4,5]triazapentalene (VIII), mp 289-291° (dec.), as colorless prisms.

Anal. Calcd for $C_{13}H_9N_3$: C, 75.61; H, 4.55; N, 19.98.

Found: C, 75.39; H, 4.72; N, 20.11.

IR (KBr) cm^{-1}: 2700-3100 (νNH).

NMR (DMSO-d_6) δ: 7.8-8.3 (m, NH and aromatic protons).

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UV λ_{max}^{EtOH} nm (log ε): 244 (4.5), 247 (4.5), 250 (4.5), 293 (3.8), 304 (4.1), 353 (4.0), 370 (3.95).

Mass spectrum m/e: 207 (M^+).

Thermolysis of VI.—A solution of 0.6 g of VI in 20 ml of xylene was refluxed for 3.5 hr. The solvent was evaporated in vacuo to leave a residue, which was purified as described above to give 0.4 g (76%) of VIII.

Photolysis of VI.— i) In the Absence of Sensitizer. A solution of 1.35 g of VI in 200 ml of benzene was irradiated by a 100W high-pressure mercury lamp with a Pyrex filter at room temperature for 2 hr. The reaction mixture was concentrated in vacuo and chromatographed on silica gel using benzene as an eluent, affording 0.8 g (63%) of VIII and trace amounts of red crystals.

Recrystallization of red crystals from ethanol gave 2,2'-di(2-indazolyl)azobenzene (IX), mp 144-145°, as red prisms.

Anal. Calcd for $C_{26}H_{18}N_6$: C, 75.55; H, 4.46; N, 20.46.

Found: C, 75.34; H, 4.38; N, 20.28.

UV λ_{max}^{EtOH} nm (log ε): 335 (4.0).

Mass spectrum m/e: 414 (M^+).

ii) In the Presence of Acetophenone as Sensitizer. Similarly, a solution of 0.7 g of VI and 40 ml of acetophenone in 160 ml of benzene was irradiated by a 100W high-pressure mercury lamp for 2 hr. By similar procedure as mentioned above, 70 mg (11%) of VIII and 0.3 g (46%) of IX were obtained.

Preparation of IX.—A solution of 1.5 g of V in 20 ml of 20% aqueous sodium hydroxide was refluxed with 10 g of zinc dust for 2 hr, and then the reaction mixture was filtered. After air had been passed through the filtrate at room temperature for 3 hr, the reaction mixture was extracted with diethyl ether. The ether extract was concentrated in vacuo, and a residue was

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recrystallized from ethanol to give 0.56 g (43%) of IX, mp 144-145°, as red prisms.

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* To whom inquiries should be addressed.

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