

Studies of Polyazapentalenes. I.
The Preparation of 6-Dehydroindazolo[1,2-*a*]benzotriazole

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Received March 23, 1971

The photolysis of 1-(*o*-azidophenyl)-1*H*-indazole (IV) has been found to give a mixture of 6-dehydroindazolo[1,2-*a*]benzotriazole (VI) and 2,2'-di(1-indazolyl)azobenzene (VII). On the other hand, 1-(*o*-nitrophenyl)-1*H*-indazole (I) was reduced with triethyl phosphite, affording VI and dibenzo[*a,i*]indazolo[1,2,3-*cd*]indazolo[3,2,1-*fg*]-3,3a,5a,6,8a,8b-hexaaza-*as*-indacene (XIa).

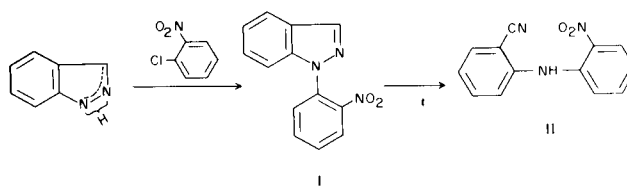
Recently, there has been great interest in non-benzoid aromatic compounds. Although the hydrocarbon pentalene, an 8 π electron system, has not been synthesized, 10 π electron azapentalenes, whose electronic configurations are isoelectronic with those of pentalenyl dianion and naphthalene, have been prepared. These include diaza- (1-3), triaza- (4), tetraaza- (5-11) and hexaazapentalenes (12). However, the only example involving triazapentalene is benzo[*a*]-1,3a,6a-triazapentalene (pyrazolo[1,2-*a*]benzotriazole) obtained by the reductive cyclization of 1-(*o*-nitrophenyl)pyrazole with triethyl phosphite (4).

In the present paper, we wish to report the photolysis of 1-(*o*-azidophenyl)-1*H*-indazole and the reductive cyclization of 1-(*o*-nitrophenyl)-1*H*-indazole with triethyl phosphite to yield dibenzo[*b,e*]-1,3a,6a-triazapentalene (6-dehydroindazolo[1,2-*a*]benzotriazole), accompanied by the azobenzene or hexaaza-*as*-indacene derivative respectively.

The arylation of indazole with *o*-chloronitrobenzene in the presence of potassium acetate and a small amount of cupric acetate gave 1-(*o*-nitrophenyl)-1*H*-indazole (I) in 52% yield. No 2-aryl isomer was isolated in the arylation. The structure of I was established by the elemental analysis and spectral studies as well as by the chemical transformation.

When I was heated with cupric acetate, 2-cyano-2'-nitrodiphenylamine (II), whose structure was confirmed by the spectral data as well as by the elemental analysis, was obtained. The production of II from I eliminated the possibility of the formation of the 2-aryl isomer. Similar phenomena have been previously observed by Tiefenthaler *et al.* (13): the photolysis of 1-alkyl (or aryl)indazole gave, by opening of the N-N bond and migration of the hydrogen atom from the 3- to the

1-position, 2-alkyl(or aryl)aminobenzonitrile, while the 2-alkyl isomers were converted into the corresponding 1-alkylbenzimidazoles.



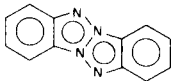
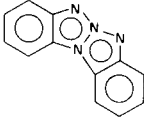
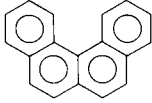
A similar reaction in the presence of sodium acetate in place of potassium acetate afforded I in 30.8% yield, accompanied by a small amount of II.

When a benzene solution of 1-(*o*-azidophenyl)-1*H*-indazole (IV), prepared from 1-(*o*-aminophenyl)-1*H*-indazole (III) in the usual manner, was irradiated by a 30W low-pressure mercury lamp with a Pyrex filter at room temperature, two crystalline compounds, one with m.p. of 158-159° and the other with m.p. of 234-235°, were obtained in 23 and 20% yields, respectively, and one molar equivalent of nitrogen was evolved.

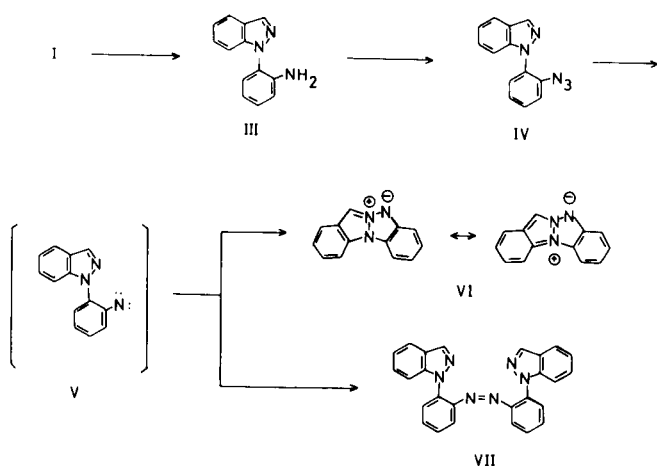
The former product was assigned the structure of 6-dehydroindazolo[1,2-*a*]benzotriazole (VI) based upon the mode of formation and the analytical and spectral data. The molecular formula of VI, C₁₃H₉N₃ (M⁺ m/e 207), was the same as that derived from IV upon elimination of nitrogen. The ir spectrum of VI did not show any bands for the NH group, while its nmr spectrum exhibited a multiplet in the region of aromatic protons (δ 7.0-8.0 ppm). These observations ruled out the possibility of cyclization to the 3- or 7-carbon of the indazole ring.

Furthermore, the uv spectrum of VI showed many of the characteristic similarities and differences that have

TABLE I
UV Spectra of VI,
Dibenzotetraazapentalenes and Benzo[*c*]phenanthrene

VI							
λ max, m μ	ϵ	λ max, m μ	ϵ	λ max, m μ	ϵ	λ max, m μ	ϵ
394	8900	402	38300	356	39700	372	250
288	2000	382	23300	343	32300	353	398
262	4160	323	4110	286	8250	315	12600
244	2900	308	2850	271	5900	281	79400
		255	63000	234	25000	218	50100

been noted (14) between aromatic heterocycles and their carbocyclic analogs. Principal absorptions of VI are given in Table I, together with those of dibenzo-tetraazapentalenes (7) and benzo[*c*]phenanthrene (15).



Scheme 1

The long wavelength absorption of VI is about 36 times more intense than the α band of benzo[*c*]phenanthrene. Similar comparisons for many aromatic azahydrocarbon-hydrocarbon combinations have been reported by Badger and his co-workers (14).

The mass spectrum of VI was also in harmony with the proposed structure: peaks appeared at m/e 207 (M^+), 181 ($M^+ -CN$), 180 ($M^+ -HCN$) and 179 ($M^+ -N_2$).

On the other hand, the second compound was identified as 2,2'-di(1-indazolyl)azobenzene (VII) by the analytical and spectral data as well as by the unequivocal synthesis from I.

As is shown in Scheme 1, it may be deduced that VI and VII are formed *via* the nitrene intermediate V, which is derived from IV upon elimination of nitrogen.

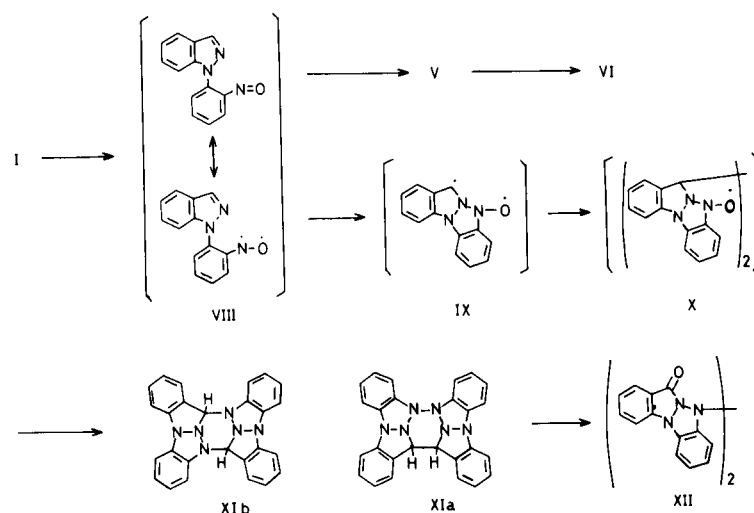
When a solution of I and triethyl phosphite in xylene was refluxed for 10 hours, two products, VI and XI (m.p. 244-245°), were obtained in 30 and 30.6% yields, respectively.

Although the results of elemental analysis and the molecular weight were consistent with those of the azobenzene VII, XI was found to be evidently different from VII. The ir spectrum of XI did not reveal any bands assignable to the NH group, while the nmr spectrum showed multiplets at δ 6.8 (2H, methine protons) and 7.35-7.7 ppm (16H, aromatic protons).

On the basis of the above observations and of the mode of formation, dibenzo[*a,i*]indazolo[1,2,3-*cd*]indazolo[3,2,1-*fg*]3,3a,5a,6,8a,8b-hexaaza- (XIa) and dibenzo[*a,i*]benzotriazolo[1,2,3-*fg*]indazolo[1,2,3-*cd*]-3,3a,5,5a,6,8b-hexaaza-*as*-indacene (XIb) are possible for the structure of XI.

The oxidation of XI with sodium dichromate in acetic acid gave XII ($C_{26}H_{16}N_2O_2$), m.p. 256-257.5°, whose ir spectrum showed the characteristic band ascribed to the CO group at 1695 cm^{-1} and nmr spectrum revealed a multiplet assignable to aromatic protons at δ 7.2-8.3 ppm. Although the molecular ion peak (M^+ m/e 444) was not observed in the mass spectrum of XII, weak peaks appeared at m/e 416 ($M^+ -CO$ or N_2), 388 ($416^+ -CO$ or N_2), 359 ($388^+ -CHO$) and 330 ($359^+ -CHO$) together with strong peaks at m/e 222 ($M^+/2$, 93), 194 ($222^+ -CO$, 51), 166 ($194^+ -N_2$, 100) and 140 ($166^+ -CN$, 51) in the spectrum (16).

In view of the above facts, it seems most reasonable to conclude that the compound XII is 6,6'-bis(12-oxoinda-



Scheme 2

zolo[1,2-*a*]benzotriazolyl), and consequently the compound XI is the 3,3a,5a,6,8a,8b-hexaaza-*as*-indacene XIa.

The structure XIa for XI was also supported by the mass spectrum: peaks of m/e 414 (M^+), 385 ($M^+ - N_2, -H$), 357 ($385 - N_2$) and 207 ($M^+/2$) appeared in the spectrum.

The dimerization of VI was not observed under the reaction condition used. Although the pathway for the formation of XIa is not clear, it is assumed that deoxygenation of I gives the nitroso compound VIII, which cyclizes to IX followed by dimerization of IX to X with subsequent deoxygenation of X to give XIa (Scheme 2).

EXPERIMENTAL (17)

1-(*o*-Nitrophenyl)-1*H*-indazole (I).

A mixture of indazole (120 g.), *o*-chloronitrobenzene (198 g.), potassium acetate (114 g.) and finely crushed cupric acetate dihydrate (0.5 g.) was stirred at 200-210° (bath temperature) for 24 hours: during this time a stream of nitrogen was slowly passed through the reaction mixture and the acetic acid formed was removed by distillation. The reaction mixture was steam distilled to remove *o*-chloronitrobenzene, and the residue was extracted with a benzene-dichloromethane mixture (1:1 vol./vol., 1500 ml.). The extract was washed with 5*N* hydrochloric acid and with water, dried over sodium sulfate, and then evaporated *in vacuo* to give a residue, which after three recrystallizations from benzene gave 130 g. (52%) of I, m.p. 152-153°, as yellow prisms; ir (potassium bromide): 1532, 1367 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 7.2-8.3 ppm (multiplet); mass spectrum: m/e 239 (M^+).

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_2$: C, 65.20; H, 3.79; N, 17.57. Found: C, 65.30; H, 3.97; N, 17.35.

2-Cyano-2'-nitrodiphenylamine (II).

After a mixture of I (100 mg.) and finely crushed cupric acetate dihydrate (50 mg.) was heated at 230° for 20 minutes, the reaction mixture was extracted with benzene. The benzene extract was chromatographed on alumina, affording 25 mg. (40%) of II,

m.p. 115-116°, as orange red prisms and 50 mg. of unreacted I; ir (potassium bromide): 3310 (NH), 2308 ($\text{C}\equiv\text{N}$), 1532, 1350 cm^{-1} (NO_2); nmr (deuteriochloroform): δ 6.4-7.4 (multiplet, 8H, aromatic protons), 8.5-8.6 ppm (multiplet, 1H, NH, exchanged with deuterium oxide); mass spectrum: m/e 239 (M^+).

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_3\text{O}_2$: C, 65.20; H, 3.79; N, 17.57. Found: C, 65.41; H, 3.57; N, 17.27.

1-(*o*-Aminophenyl)-1*H*-indazole (III).

To a vigorously stirred suspension of I (2 g.) and iron powder (16 g.) in ethanol (100 ml.), a solution of concentrated hydrochloric acid (5 ml.) and ethanol (40 ml.) was added dropwise, under reflux, over a period of 2 hours. The reaction mixture was refluxed for an additional hour, and filtered. The filtrate was made slightly basic with aqueous potassium hydroxide solution and then refiltered. Evaporation of the filtrate *in vacuo* gave crystals, which on crystallization from water gave 1.5 g. (87%) of III, m.p. 75-76°, as colorless needles; ir (potassium bromide): 3470, 3380 cm^{-1} (NH); mass spectrum: m/e 209 (M^+).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{N}_3$: C, 74.62; H, 5.30; N, 20.08. Found: C, 74.38; H, 5.36; N, 19.83.

1-(*o*-Azidophenyl)-1*H*-indazole (IV).

A solution of sodium nitrite (0.9 g.) in 10 ml. of water was added dropwise to a stirred mixture of III (2 g.), concentrate hydrochloric acid (15 ml.) and ice-water (20 g.) at 0 ~ -5° over a period of 30 minutes, and stirring was continued for an additional hour after the nitrite addition. Sodium azide (1.4 g.) in 10 ml. of water was slowly added to the diazonium solution at 5° with continued stirring: during this time nitrogen evolved, and the mixture became viscous. The mixture was stirred for an additional 2 hours, and then extracted with diethyl ether. The ether extract was dried over sodium sulfate and evaporated *in vacuo*, leaving a viscous oil, which on chromatography on alumina using benzene as eluent gave 1.3 g. (59%) of IV as a viscous yellow oil; ir (neat): 2180 cm^{-1} (N_3); mass spectrum: m/e 235 (M^+).

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{N}_5$: C, 66.37; H, 3.86; N, 29.77. Found: C, 66.33; H, 3.83; N, 29.62.

Photolysis of IV.

A solution of IV (0.5 g.) in benzene (300 ml.) was irradiated by a 30W low-pressure mercury lamp with a Pyrex filter at room temperature for 6 hours: during this time the theoretical amount (about 50 ml.) of nitrogen was evolved. The reaction mixture was concentrated *in vacuo* and chromatographed on silica gel using benzene as eluent, affording 100 ml. (23%) of 6-dehydroindazolo-[1,2-*a*]benzotriazole (VI) and 90 mg. (20%) of 2,2'-di(1-indazolyl)-azobenzene (VII).

Recrystallization of VI from petroleum benzin (b.p. 60-90°) gave yellow prisms, m.p. 158-159°.

Anal. Calcd. for C₁₃H₉N₃: C, 75.34; H, 4.38; N, 20.28. Found: C, 75.61; H, 4.55; N, 19.98.

Recrystallization of VII from methanol gave orange yellow prisms, m.p. 234-235°; uv (ethanol): λ max 331 mμ (log ε 3.8); mass spectrum: m/e 414 (M⁺, 65), 221 (24), 193 (221⁺-N₂, 100), 166 (193⁺-HCN, 25) (16).

Anal. Calcd. for C₂₆H₁₈N₆: C, 75.34; H, 4.38; N, 20.28. Found: C, 75.21; H, 4.32; N, 20.04.

This compound was identical with an authentic sample prepared by the following manner. A solution of I (1.5 g.) in 20% aqueous sodium hydroxide (20 ml.) was refluxed with zinc dust (10 g.) for 2 hours, and then the reaction mixture was filtered. After air had been passed through the filtrate at room temperature for 3 hours, the reaction mixture was extracted with diethyl ether. The ether extract was concentrated *in vacuo*, and a residue was recrystallized from methanol to give 0.8 g. (60%) of VII, m.p. 234-235°.

Reaction of I with Triethyl Phosphite.

After a solution of I (5.0 g.) and triethyl phosphite (12.5 g.) in xylene (50 ml.) was refluxed for 10 hours, the reaction mixture was evaporated *in vacuo* to leave a residue, which was extracted with diethyl ether. The ether extract was evaporated and the crystals were purified by chromatography on silica gel using benzene as eluent and the subsequent recrystallization from petroleum benzin (b.p. 60-90°), affording 1.3 g. (30%) of VI, m.p. 158-159°.

Recrystallization of the ether-insoluble residue from benzene gave 1.32 g. (30.6%) of the 3,3a,5a,6,8a,8b-hexaaza-as-indacene (XIa), m.p. 244-245°, as pale yellow prisms; uv (ethanol); λ max mμ (log); 244 (3.95), 288 (4.1).

Anal. Calcd. for C₂₆H₁₈N₆: C, 75.34; H, 4.38; N, 20.28. Found: C, 75.27; H, 4.49; N, 20.07.

Oxidation of XIa.

A solution of XIa (100 mg.) and sodium dichromate (500 mg.) in acetic acid (10 ml.) was refluxed for 24 hours. The reaction

mixture was poured into water and the precipitated solid was collected by filtration. Recrystallization from acetone gave 45 mg. (42%) of 6,6'-bis(12-oxoindazolo[1,2-*a*]benzotriazolyl) (XII), m.p. 256-257.5°, as pale yellow prisms.

Anal. Calcd. for C₂₆H₁₆N₆O₂: C, 70.26; H, 3.63; N, 18.91. Found: C, 70.53; H, 3.59; N, 18.75.

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- (16) Figures in parentheses indicate the relative intensities of peaks in the mass spectrum.
- (17) Melting points are uncorrected. The ir spectra were recorded on a Nippon Bunko IR-S spectrophotometer, while the uv spectra were measured with a Shimadzu SV-50A spectrophotometer. The nmr spectra were determined in a deuteriochloroform solution at 60 HMz with a Hitachi R-20 nmr spectrometer, using TMS as the internal reference.