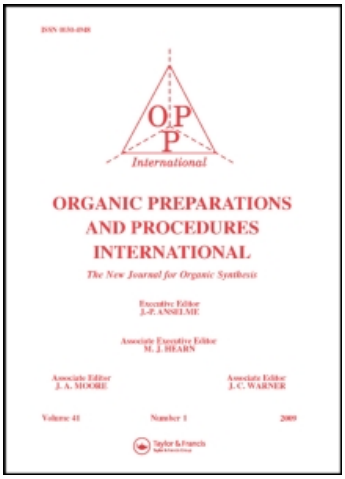

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STUDIES OF POLYAZAPENTALENES. II. THE PREPARATION OF 1,3a, 6a-TRIAZAPENTALENES

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STUDIES OF POLYAZAPENTALENES. II.[1]

THE PREPARATION OF 1,3a,6a-TRIAZAPENTALENES

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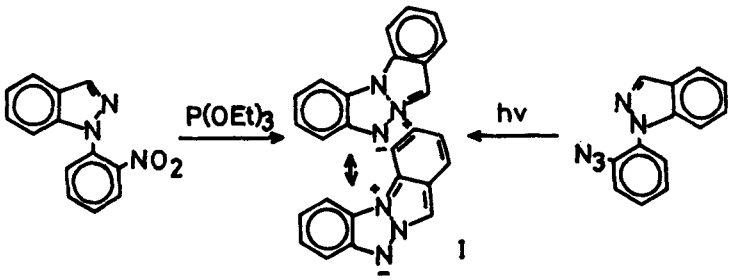
We previously reported[1] the preparation of a new aromatic system, 5,7-dehydro-5H,7H-indazolo[1,2-a]benzotriazole (dibenzo[b,e]-1,3a,6a-triazapentalene) (I), by the reductive cyclization of 1-(o-nitrophenyl)-1H-indazole with triethyl phosphite or by the photolysis of 1-(o-azidophenyl)-1H-indazole.

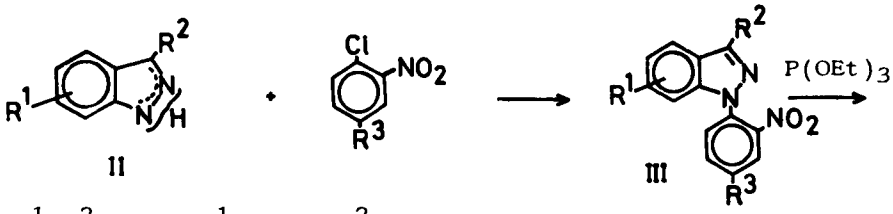


I

During the course of an investigation of some reactions of triazapentalene I, it became desirable to find more stable and tractable triazapentalenes, because I is rather unstable. Furthermore, it appeared of interest to investigate the effect of substituents on the properties of the dibenzo-1,3a,6a-triazapentalene system. We attempted therefore to synthesize substituted dibenzo-1,3a,6a-triazapentalenes by the reductive cyclization of 1-(o-nitrophenyl)-1H-indazoles with triethyl phosphite.

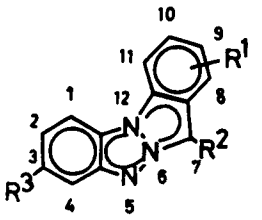
The arylations of indazoles (II) with o-chloronitrobenzenes were carried out in a manner similar to that of indazole.[1] The reaction of indazoles (II) with o-chloronitrobenzenes in the presence of potassium acetate and small amounts of cupric acetate gave the corresponding 1-(o-nitrophenyl)-1H-indazoles (III); none of the 2-aryl isomers were isolated.

When a solution of III and triethyl phosphite in xylene was refluxed for 10 hr under a stream of nitrogen, the expected triazapentalene IV and/or dimer V of IV were obtained. Reductive cyclizations of 1-(o-nitrophenyl)-4-methyl- (IIIa), -6-methyl- (IIIc), -3-methyl- (IIId) and -4-chloro-1H-indazole (IIIe) gave only the corresponding triazapentalenes (IVa, IVc-IVe) and 5-methyl derivative (IIIb) afforded triazapentalene IVb and dimer Va in almost equal yields. However, the reaction



a: $R^1=R^2=H$; b: $R^1=4\text{-Me}$, $R^2=H$;
c: $R^1=5\text{-Me}$, $R^2=H$; d: $R^1=6\text{-Me}$, $R^2=H$;
e: $R^1=H$, $R^2=Me$; f: $R^1=4\text{-Cl}$, $R^2=H$

a: $R^1=4\text{-Me}$, $R^2=R^3=H$
b: $R^1=5\text{-Me}$, $R^2=R^3=H$
c: $R^1=6\text{-Me}$, $R^2=R^3=H$
d: $R^1=R^3=H$, $R^2=Me$
e: $R^1=4\text{-Cl}$, $R^2=R^3=H$
f: $R^1=R^2=H$, $R^3=Me$



and/or Dimer (V)

a: $R^1=8\text{-Me}$, $R^2=R^3=H$; d: $R^1=R^3=H$, $R^2=Me$
b: $R^1=9\text{-Me}$, $R^2=R^3=H$; e: $R^1=8\text{-Cl}$, $R^2=R^3=H$
c: $R^1=10\text{-Me}$, $R^2=R^3=H$

of 1-(2-nitro-4-methylphenyl)-1H-indazole (IIIf) yielded dimer Vb as the sole product and none of the corresponding triazapentalene could be isolated.

The structures of all triazapentalenes (IV) were established on the basis of analytical and spectral data. The yields, physical properties and results of microanalyses of IV are given in Table 1.

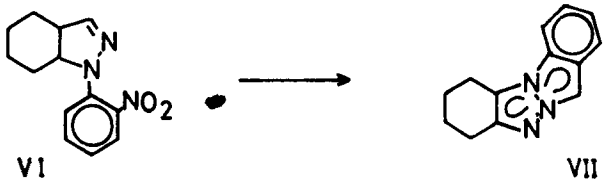
Table 1. 1,3a,6a-Triazapentalenes[a)]

	Yield %	Mp. °C	NMR($CDCl_3$), δ ppm CH_3	Aromatic	Anal. Found(Calcd) C	H	N	M^+
IVa	33	190-191(dec)	2.79 (s, 3H)	6.8-7.8 (m, 8H)	76.21 (75.99)	4.90 (5.01)	19.26 (18.99)	221
IVb	11	188-189(dec)	2.70 (s, 3H)	6.7-7.8 (m, 8H)	76.21 (75.99)	5.23 (5.01)	19.15 (18.99)	221
IVc	24	142-143(dec)	2.50 (s, 3H)	6.7-7.8 (m, 8H)	76.03 (75.99)	4.98 (5.01)	19.28 (18.99)	221
IVd	32	125-126	2.54 (s, 3H)	6.7-7.6 (m, 8H)	75.81 (75.99)	4.89 (5.01)	19.26 (18.99)	221
IVe	32	197-198	———	6.7-7.8 (m)	64.60 (64.60)	3.61 (3.73)	17.70 (17.39)	241 243
VII	12.5	149-150	1.6-2.2 2.5-3.1 (each, CH_2)	6.8-7.6 (m, 5H)	75.49 (75.90)	6.50 (6.20)	19.89 (19.89)	211

a) All triazapentalenes are yellow needles.

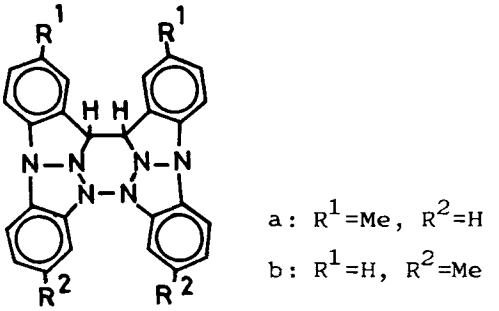
Similarly, the reductive cyclization of 1-(o-nitrophenyl)-tetrahydro-1H-indazole (VI) which was prepared from the arylation of tetrahydro-1H-indazole, afforded the corresponding triazapentalene VII. The yield, physical properties and re-

sults of microanalysis of VII are included in Table 1.



VI VII

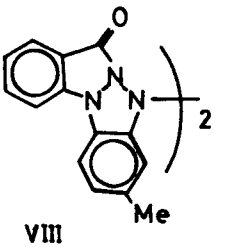
The structures of dimers Va and Vb can be viewed to be that of dibenzo[a,i]indazolo[1,2,3-cd]indazolo[3,2,1-fg]-3,3a,5a,6-8a,8b-hexaaza-as-indacene, formed in the reductive cyclization of 1-(o-nitrophenyl)-1H-indazole.[1] The IR spectra of these three dimers are very similar to each other and did not exhibit any NH bands. The NMR spectra of Va and Vb showed signals ascribable to methyl, methine and aromatic protons. Furthermore, the oxidation of Vb with sodium dichromate in acetic acid gave



V

a: R^1=Me, R^2=H

b: R^1=H, R^2=Me



VIII

5,5'-bis(3-methyl-7-oxoindazolo[1,2-a]benzotriazolyl) (VIII), whose structure was assigned on the basis of spectral data as well as on the results of microanalysis.

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-4 mass spectrometer using a direct inlet and an ionization energy at 70 eV. The IR spectra were measured as KBr discs. The microanalyses were performed by Miss M. Akita of our laboratory.

Indazoles (II).—4-Methyl- (IIb), mp. 115-116° (42% yield), 5-methyl- (IIc), mp. 116-117° (lit.[3] mp. 117°), (20% yield), 6-methyl- (IId), mp. 117-118° (lit.[3] mp. 117-118°), (25% yield) and 4-chloroindazole (IIf), mp. 155-156° (lit.[4] mp. 156°), (46% yield) were prepared from the corresponding substituted o-toluidines according to the reported method of the synthesis of indazole (IIa).[5]

4-Methylindazole (IIb):

Anal. Calcd. for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20.
Found: C, 72.83; H, 6.20; N, 21.35.

NMR($CDCl_3$) δ ppm: 2.55 (3H, s, CH_3), 6.7-7.3 (3H, aromatic protons), 8.06 (1H, s, =CH-), 11.24 (1H, s, NH).

Mass spectrum m/e: 132 (M^+).

3-Methylindazole (IIe), mp. 112° (lit.[6] mp. 112°), (50% yield) and 4,5,6,7-tetrahydroindazole, mp. 78-80° (lit.[7] mp. 79-80°), (97% yield) were obtained by reported methods.[6,7]

Arylation of Indazoles (II).—A typical procedure is illustrated by the reaction of 4-methylindazole (IIb) with o-chloronitrobenzene. A mixture of 80 g (0.61 mol) of IIb, 114 g (0.73 mol) of o-chloronitrobenzene, 73 g (0.73 mol) of potassium acetate and 0.5 g of finely powdered cupric acetate monohydrate was stirred at 210-220° (bath temperature) for 24 hr during which time a stream of nitrogen was slowly passed through the reaction mixture; the acetic acid formed was re-

moved by distillation. The reaction mixture was steam distilled to remove excess o-chloronitrobenzene and the residue was extracted with 1 l. of dichloromethane. The extract was washed with water, dried over calcium chloride, and then evaporated in vacuo. A solution of the residue in benzene was treated with active charcoal to remove resinous materials and concentrated in vacuo. Several recrystallizations from benzene gave 36 g (23%) of 1-(o-nitrophenyl)-4-methyl-1H-indazole (IIIa), mp. 136-137°, as yellow prisms.

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59.
Found: C, 66.10; H, 4.23; N, 16.88.

IR cm^{-1}: 1539, 1365 (ν_{NO_2}). Mass spectrum m/e: 253 (M^+).
NMR ($CDCl_3$) δ ppm: 2.58 (3H, s, CH_3), 6.8-8.3 (7H, m, aromatic protons), 8.35 (1H, s, =CH-).

Similarly, other 1-aryl-1H-indazoles were prepared by the arylation of the corresponding indazoles.

1-(o-Nitrophenyl)-5-methyl-1H-indazole (IIIb), mp. 117-118°, yellow prisms, 15% yield.

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59.
Found: C, 66.26; H, 4.15; N, 16.61.

IR cm^{-1}: 1540, 1370 (ν_{NO_2}). Mass spectrum m/e: 253 (M^+).
NMR($CDCl_3$) δ ppm: 2.47 (3H, s, CH_3), 7.2-8.05 (7H, m, aromatic protons), 8.08 (1H, s, =CH-).

1-(o-Nitrophenyl)-6-methyl-1H-indazole (IIIc), mp. 124-125°, yellow prims, 12% yield.

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59.
Found: C, 66.51; H, 4.49; N, 16.81.

IR cm^{-1}: 1540, 1362 (ν_{NO_2}). Mass spectrum m/e: 253 (M^+).
NMR($CDCl_3$) δ ppm: 2.45 (3H, s, CH_3), 6.8-8.0 (7H, m, aromatic

protons), 8.07 (1H, s, =CH-).

1-(-o-Nitrophenyl)-3-methyl-1H-indazole (IIId), mp. 126-127°, yellow prisms, 58% yield.

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59.
Found: C, 66.26; H, 4.35; N, 16.65.

IR cm^{-1}: 1530, 1368 (ν_{NO_2}). Mass spectrum m/e: 253 (M^+).

NMR($CDCl_3$) δ ppm: 2.57 (3H, s, CH_3), 7.0-8.05 (8H, m, aromatic protons).

1-(o-Nitrophenyl)-4-chloro-1H-indazole (IIIe), mp. 150-151°, yellow prisms, 31% yield.

Anal. Calcd. for $C_{13}H_9N_3O_2Cl$: C, 57.04; H, 3.29; N, 15.36.
Found: C, 57.23; H, 3.29; N, 15.08.

IR cm^{-1}: 1540, 1368 (ν_{NO_2}).

Mass spectrum m/e: 273, 275 (M^+, rel. intensity 3:1).

1-(2-Nitro-4-methylphenyl)-1H-indazole (IIIf), mp. 116-117°, yellow prisms, 18.4% yield.

Anal. Calcd. for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59.
Found: C, 66.21; H, 4.10; N, 16.83.

IR cm^{-1}: 1520, 1375 (ν_{NO_2}). Mass spectrum m/e: 253 (M^+).

1-(o-Nitrophenyl)-4,5,6,7-tetrahydro-1H-indazole (VI), mp. 94-96°, pale yellow prisms, 44% yield.

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.18; H, 5.39; N, 17.78.
Found: C, 64.42; H, 5.47; N, 17.68.

IR cm^{-1}: 1540, 1370 (ν_{NO_2}). Mass spectrum m/e: 243 (M^+).

NMR($CDCl_3$) δ ppm: 1.6-2.1, 2.5-2.9 (each 4H, m, CH_2), 7.2-8.1 (5H, m, aromatic protons).

Reaction of 1-(o-Nitrophenyl)-5-methyl-1H-indazole (IIIb) with Triethyl phosphite.— A typical run of the reductive cycli-

zation of III is illustrated by the reaction of IIIb. After a solution of 1.0 g (4.2 mmol) of IIIb and 2.5 g (14.6 mmol) of triethyl phosphite in 10 ml of xylene had been refluxed for 10 hr under a stream of nitrogen, the reaction mixture was evaporated in vacuo to leave a residue, which was extracted with 50 ml of diethyl ether. The ethereal extract was evaporated and the crystals were purified by chromatography on silica gel using benzene as eluent. Recrystallization from pet. ether afforded 0.1 g (11%) of 9-methyldibenzo[b,e]-1,3a,6a-triazapentalene (IVb).

Recrystallization of the ether-insoluble residue from toluene gave 0.1 g (11%) of dimer Va, mp. 248-250° (dec), as pale yellow prisms.

Anal. Calcd. for $C_{28}H_{22}N_6$: C, 75.99; H, 5.01; N, 18.99.
Found: C, 76.23; H, 4.86; N, 18.71.

Mass spectrum m/e: 442 (M^+).

NMR($CDCl_3$) δ ppm: 2.33 (6H, s, CH_3), 6.64 (2H, $\geq CH$), 7.1-8.3 (14H, m, aromatic protons).

Dimer Vb. A similar reaction of 7.5 g (30 mmol) of 1-(2-nitro-4-methylphenyl)-1H-indazole (IIIf) with 17.4 g (105 mmol) of triethyl phosphite in 20 ml of xylene afforded 3.0 g (45%) of dimer Vb, mp. 199-200° (dec), as pale yellow prisms.

Anal. Calcd. for $C_{28}H_{22}N_6$: C, 75.99; H, 5.01; N, 18.99.
Found: C, 76.25; H, 4.75; N, 19.23.

Mass spectrum m/e: 442 (M^+).

NMR($CDCl_3$) δ ppm: 2.57 (6H, s, CH_3), 6.78 (2H, $\geq CH$). 7.2-7.5 (12H, aromatic protons).

Oxidation of dimer Vb.—A solution of 0.5 g of Vb and 2.5 g of

sodium dichromate in 20 ml of acetic acid was refluxed for 20 hr. The reaction mixture was poured into water and the precipitated solid was collected by filtration. Recrystallization from acetone afforded 0.3 g (56%) of 5,5'-bis(3-methyl-7-oxoindazolo[1,2-a]benzotriazolyl) (VIII), mp. 225° (dec), as pale yellow prisms.

Anal. Calcd. for $C_{28}H_{20}N_6O_2$: C, 71.17; H, 4.27; N, 17.79.
Found: C, 71.01; H, 4.45; N, 17.51.

IR cm^{-1}: 1690 (ν_{CO}).

Mass spectrum m/e (rel. intensity %): 472 (M^+, +), 444 (M^+ - CO, 4), 416 (444^+ - CO, 11), 236 ($M^+/2$, 90), 208 (236^+ - CO, 92), 180 (208^+ - N_2, 100).

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