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SYNTHESIS OF INDAZOLES USING POLYPHOSPHORIC ACID—I

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Abstract—Indazoles have been synthesized from nitrophenyl-hydrazones of several acetophenones, benzaldehydes and benzophenones, employing polyphosphoric acid as catalyst.

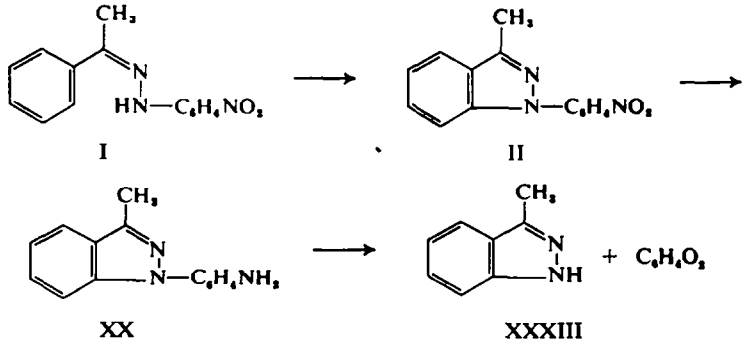
WHEN the *p*-nitrophenylhydrazones of several acetophenones were treated with polyphosphoric acid (PPA) at 150–165°, new substances containing the three original nitrogen atoms were isolated from the reaction, which were characterized as nitrophenylindazoles.[1]

In all cases a marked darkening was observed at the temperature needed to produce the reaction and the formation of much tar takes place. Any attempt to increase the yields by increasing the temperature failed, although the pure nitrophenylindazoles formed are rather stable when submitted to a similar treatment with PPA.

This action of PPA is rather specific, because when it was substituted by 20% sulphuric acid or conc hydrochloric acid, the *p*-nitrophenylhydrazones were recovered. The presence of the nitro group is necessary for the reaction, because the phenylhydrazones of acetophenones gave the expected indoles on treatment with PPA.[2]

Proof of the formation of an indazole nucleus was obtained with certainty in the case of the product resulting from acetophenone *p*-nitrophenylhydrazone (I) by transformation into the known 3-methylindazole (XXXIII) through a series of reactions.

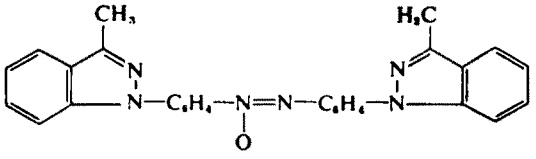
The 1-*p*-nitrophenyl-3-methylindazole (II) was reduced to the corresponding amino compound (XX) which, when carefully oxidized in aqueous solution, produces *p*-benzoquinone and the indazole (XXXIII) identical to that prepared by Fischer and Tafel[3] by a direct method of synthesis.



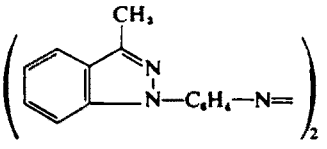
* Research Fellow of the Consejo Nacional de Investigaciones Cientlficas y Técnicas.

[1] For a preliminary communication see A. R. Frasca, *Tetrahedron Letters* 1115 (1962).
[2] E. B. Dennler, *Doctoral Thesis*, University of Buenos Aires (1965).
[3] E. Fischer and J. Tafel, *Liebigs Ann.* **227**, 303 (1885).

Treatment of the 1-*p*-nitrophenyl-3-methylindazole (II) with ethanolic potassium hydroxide, or reduction with potassium borohydride yielded the expected azoxybenzene (XXXI), while reduction with LAH produced the azobenzene (XXXII).



XXXI



XXXII

In this paper we report the application of this reaction to a series of *p*-nitrophenylhydrazones of different acetophenones and to a few derived from benzaldehydes and benzophenones. The results are summarized in Tables 1 and 2.

The method of elimination of the *p*-nitrophenyl group, previously described, was applied to some of the condensation products from substituted acetophenones. The amines (Table 3) and indazoles (Table 4) thus obtained, showed a chemical behaviour and an UV spectrum in agreement with the proposed structures.

The properties of the compounds formed from the remaining acetophenones, benzaldehydes and benzophenones employed leave no doubt that they also have the 1-nitrophenylindazole structure.

For most of the carbonyl compounds used, the substitution on the benzene ring can lead to only one indazole with definite structure. In a few exceptional cases, two isomeric indazoles can be obtained, although notwithstanding this possibility, only one was detected by chromatography and isolated. Their structure was determined in each case.

That the indazole derived from 3,4-dimethoxyacetophenone was the 1-*p*-nitrophenyl-3-methyl-5,6-dimethoxyindazole (XIV) and not the isomeric 6,7-dimethoxy derivative, resulted from the elimination of the *p*-nitrophenyl group, when a 3-methyldimethoxyindazole was obtained, whose NMR spectrum showed the presence of two isolated aromatic protons, with signals at τ 2·90 and τ 3·06, which is only compatible with the presence of the methoxy groups at the positions 5 and 6.

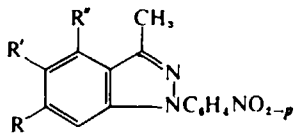
The veratraldehyde *p*-nitrophenylhydrazone produces only the 1-*p*- nitrophenyl-5,6-dimethoxyindazole (XVII). It was transformed into the 5,6-dimethoxyindazole (XXIX) whose NMR spectrum showed, as in the former case, two isolated aromatic protons at τ 2·87 and τ 2·98. Besides, its UV spectrum overlaps with that of 3-methyl-5,6-dimethoxyindazole (XXX), already described.

Substitution takes place at the same carbon atom when vanillin is employed, because methylation of the indazole formed (XVI) affords the same 1-*p*-nitrophenylindazole obtained from veratraldehyde.

The formation of indazoles from the *p*-nitrophenylhydrazones of acetophenones, under the action of PPA, is considered to be a nucleophilic substitution at the carbon atom of the benzene ring by the nitrogen atom of the phenylhydrazone.

The substitution takes place through the electronic displacements shown in Fig. 1, which are favoured by the protonation of the hydrazone at the N-2 atom. The intermediate formed (a) is transformed into the indazole by losing two hydrogen atoms. For their elimination two possible sequences can be postulated, (a → b → c

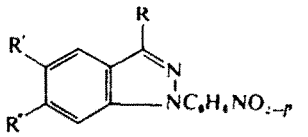
TABLE 1. 1-*p*-NITROPHENYL-INDAZOLES FROM *p*-NITROPHENYLHYDRAZONES OF ACETOPHENONES



	Compound	Yield %	m.p.	React. temp.	Formula	Analysis Found/required C	H	N	Hal.	λ max mμ (log ε)
II	R = R′ = R″ = H	29	150°[a]	160°	$C_{14}H_{11}N_3O_2$	66·20 66·39	4·56 4·38	16·33 16·61		232 (4·30), 355 (4·25)
III	R = R′ = H R″ = Cl	7	176–177°[a]	160°	$C_{14}H_{10}ClN_3O_2$	58·20 58·45	3·71 3·51	14·51 14·60	12·08 12·32	227 (4·19), 267 (3·70) 346 (4·17)
IV	R = Cl R′ = R″ = H	8	172–173°[a]	160°	$C_{14}H_{10}ClN_3O_2$	58·31 58·45	4·15 3·51	14·29 14·60	12·53 12·32	230 (4·25), 269 (3·74) 343 (4·22)
V	R = Br R′ = R″ = H	8	180–181°[b]	160°	$C_{14}H_{10}BrN_3O_2$	50·44 50·61	2·83 3·04	12·67 12·65	23·80 24·06	231 (4·52), 268 (3·88) 344 (4·31)
VI	R = Me R′ = R″ = H	42	158–159°[a]	160°	$C_{15}H_{13}N_3O_2$	67·33 67·39	4·95 4·90	15·26 15·72		216 (4·27), 236 (4·26) 266 (3·87), 356 (4·32)
VII	R = Et R′ = R″ = H	30	125–126°[a]	160°	$C_{16}H_{15}N_3O_2$	68·55 68·31	5·49 5·37	14·67 14·94		234 (4·27), 258 (3·87) 355 (4·22)
VIII	R = OMe R′ = R″ = H	47	209–210°[c]	160°	$C_{15}H_{13}N_3O_3$	63·62 63·59	4·62 4·62	14·83 14·84		231 (4·24), 276–80 (3·82) 352 (4·09)
IX	R = OEt R′ = R″ = H	40	177–178°[a]	150°	$C_{16}H_{15}N_3O_3$	64·67 64·63	5·37 5·08	13·87 14·14		232 (4·35), 276–80 (3·94) 353 (4·19)
X	R = Ph R′ = R″ = H	20	196–197°[d]	160°	$C_{20}H_{15}N_3O_2$	73·28 72·94	4·72 4·59	13·05 12·76		216 (4·23), 247 (4·42) 280 (4·08), 356 (4·21)
XI	R = OAc R′ = R″ = H	5	226–227°[e]	150°	$C_{16}H_{13}N_3O_4$	61·62 61·73	4·55 4·21	12·94 13·50		231 (4·23), 258 (3·71) 345 (4·12)
XII	R = R″ = Me R′ = H	31	167–168°[a]	165°	$C_{16}H_{15}N_3O_2$	68·39 68·31	5·78 5·37	14·66 14·94		215 (4·37), 236 (4·26) 266 (3·96), 361 (4·25)
XIII	R = R″ = OMe R′ = H	6	206–207°[a]	160°	$C_{16}H_{15}N_3O_4$	61·80 61·33	4·71 4·83	13·18 13·41		228 (4·19), 265 (3·98) 361 (4·01)
XIV	R = R′ = OMe R″ = H	25	212–213°[a]	160°	$C_{16}H_{15}N_3O_4$	61·16 61·33	5·00 4·83	13·71 13·42		215 (4·17), 240 (4·23) 265 (3·96), 305 (3·89) 365 (4·21)

Recrystallization solvents: [a] EtOH; [b] acetone; [c] benzene; [d] EtOH–chf. [e] AcOEt.

TABLE 2. 1-*p*-NITROPHENYL-INDAZOLES FROM *p*-NITROPHENYLHYDRAZONES OF BENZALDEHYDES AND BENZOPHENONES



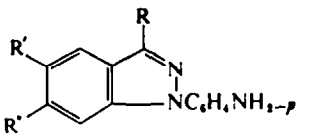
	Compound	Yield %	m.p.	React. temp.	Formula	Analysis Found/required C	H	N	λ max mμ (log ε)
XV	R = R′ = H R″ = OMe	25	172–173°[a]	150°	$C_{14}H_{11}N_3O_3$	62·56	4·06	15·79	228 (4·34), 280 (4·04)
						62·46	4·12	15·60	342 (4·21)
XVI	R = H R′ = OMe R″ = OH	15	207–208°[a]	160°	$C_{14}H_{11}N_3O_4$	59·02	3·90	14·89	237 (4·08), 262 (3·95)
						58·95	3·88	14·73	300 (3·87), 355 (4·12)
XVII	R = H R′ = R″ = OMe	40[b]	210–211°[a]	140°	$C_{15}H_{13}N_3O_4$	60·11	4·61	13·87	236 (4·16), 299 (3·93)
						60·18	4·38	14·04	350 (4·15)
XVIII	R = Ph R′ = R″ = H	30	160–161°[a,c]	150°	$C_{19}H_{13}N_3O_2$	72·18	4·03	13·21	231 (4·47), 307 (3·84)
						72·37	4·16	13·33	361 (4·32)
XIX	R = PhOMe-*p* R′ = H R″ = OMe	1	206–207°[a]	160°	$C_{21}H_{17}N_3O_4$	66·95	4·77	11·40	241 (4·28), 288 (4·08)
						67·19	4·57	11·19	367 (4·12)

[a] Crystallized from EtOH.

[b] The solid obtained by dilution of the reaction mixture was filtered and suspended in 5% NaOH, boiling it over 5 min. and following afterwards the usual technique.

[c] W. Gladstone and R. Norman gave m.p. 161–162°, *J. Chem. Soc.* 3048 (1965).

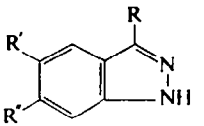
TABLE 3. 1-*p*-AMINOPHENYL-INDAZOLES



Compound		Yield %	m.p.	Formula	Analysis Found/required C	H	N	Hal.	λ max mμ (log ε)
XX	R = Me R′ = R″ = H	80	120–121°[a,c]	$C_{14}H_{13}N_3$	75·50	5·68	18·90		216 (4·22), 258 (4·08)
					75·32	5·87	18·81		303 (3·75)
XXI	R = Me R′ = H R″ = Br	80	124–125°[b]	$C_{14}H_{12}BrN_3$	55·65	3·87	14·14	26·41	220 (4·40), 264 (4·30)
					55·64	4·01	13·91	26·44	228–297 (3·83)
XXII	R = R″ = Me R′ = H	85	114–115°[a]	$C_{15}H_{15}N_3$	75·95	6·36	17·58		214 (4·50), 262 (4·30)
					75·91	6·37	17·72		305 (3·91)
XXIII	R = Me R′ = H R″ = OMe	90	111–112°[b]	$C_{15}H_{15}N_3O$	70·99	5·81	16·48		218 (4·39), 264 (4·37)
					71·12	5·97	16·59		290 (3·96)
XXIV	R = H R′ = R″ = OMe	80	217–219°[a]	$C_{15}H_{15}N_3O_2$	66·72	5·80	15·00		265 (4·30), 301 (3·75)
					66·90	5·62	15·60		
XXV	R = Me R′ = R″ = OMe	80	150–151°[a]	$C_{16}H_{17}N_3O_2$	67·25	5·83	14·34		262 (4·27), 297 (3·93)
					67·82	6·05	14·83		

Recrystallization solvents: [a] benzene–light petroleum; [b] EtOH-water; [c] Another crystalline form was obtained m.p. 136–137°.

TABLE 4. INDAZOLES



Compound		Yield %	m.p.	Formula	Analysis Found/required C	H	N	Hal.	λ max mμ (log ε)
XXVI	R = Me R′ = H R″ = Br	50	191–192°[a]	$C_8H_7BrN_2$	45·27	3·42	13·28	38·01	255 (4·64), 294–295 (3·73)
					45·52	3·34	13·28	37·86	303 (3·68)
XXVII	R = R″ = Me R′ = H	65	148–149°[a]	$C_9H_{10}N_2$	73·94	7·01	18·88		215 (4·57), 267 (3·60)
					73·93	6·89	19·18		290 (3·66), 299 (3·59)
XXVIII	R = Me R′ = H R″ = OMe	55	168–169°[b]	$C_9H_{10}N_2O$	66·77	6·21	17·20		216 (4·45), 282–287 (3·83)
					66·64	6·21	17·27		294 (3·81)
XXIX	R = H R′ = R″ = OMe	55	175°[c]	$C_9H_{10}N_2O_2$	61·01	5·83	15·35		215 (4·20), 267 (3·69)
					60·66	5·66	15·72		294 (3·79), 305 (3·67)
XXX	R = Me R′ = R″ = OMe	40	164–165°[c]	$C_{10}H_{12}N_2O_2$	62·63	6·45	14·40		216 (4·30), 267 (3·65)
					62·47	6·29	14·58		297 (3·74), 308 (3·63)

Recrystallization solvents: [a] EtOH–water; [b] benzene–light petroleum; [c] this product was purified by sublimation.

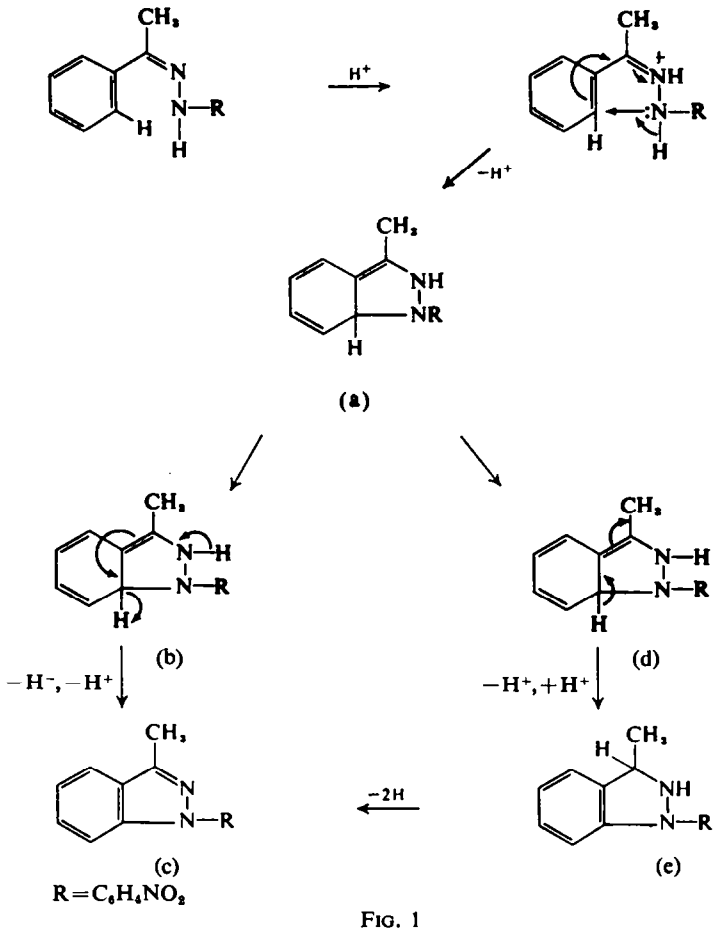


FIG. 1

and a → d → e → c), although none of them has an experimental proof. Notwithstanding the unknown process of dehydrogenation, it is possible to recognize the nitro group or some intermediate as the hydrogen acceptor.

As can be seen in Table 1, substituents with +I and/or +M effect favour the reaction and increase the yields (CH_3; C_2H_5; OCH_3; OC_2H_5), while those with contrary effects decrease them (*p*-Cl; *p*-Br; *p*-CH_3COO). Indazoles could not be isolated when the substituents were NO_2 and OH. Undoubtedly one of the factors contributing to this negative result is that in the acidic medium employed they can be protonated and decrease the facility of the displacement. The phenyl group gave a yield of the same order as when no substituent was present, in agreement with its properties shown in other reactions.

In the case of disubstituted acetophenones it was observed that while the 2,4-dimethylacetophenone *p*-nitrophenylhydrazone gives a nitrophenylindazole (XII) with a yield of the same order as the indazole (VI) derived from 4-methylacetophenone, the 2,4-dimethoxy derivative affords an indazole (XIII) with a much lower yield than that obtained from 4-methoxyacetophenone (VIII). On the other hand, the corresponding indazole (XIV) from 3,4-dimethoxyacetophenone was obtained with a better yield.

Some *p*-nitrophenylhydrazones of benzaldehydes and benzophenones also give indazoles, but other factors must play a deciding role in determining the possibility and extent of the reaction, and finally, influencing the yields, as can be seen from data in Table 2.

When some *m*-nitrophenylhydrazones of acetophenones, selected because of the typical behaviour of their substituents (H, Cl, CH_3), were treated with PPA, simultaneous formation of indazole and indoles was observed (Fig. 2). In two cases (*p*-CH_3- and *p*-Cl-acetophenones) it was even possible to isolate the two isomeric indoles expected (4-NO_2, 6-NO_2). The position of the nitro group was assigned on the basis of the UV spectra, which permits a clear differentiation between them.[4,5] On the other hand, neither indazoles nor indoles were obtained when the *o*-nitrophenylhydrazones of the same acetophenones were submitted to identical conditions.

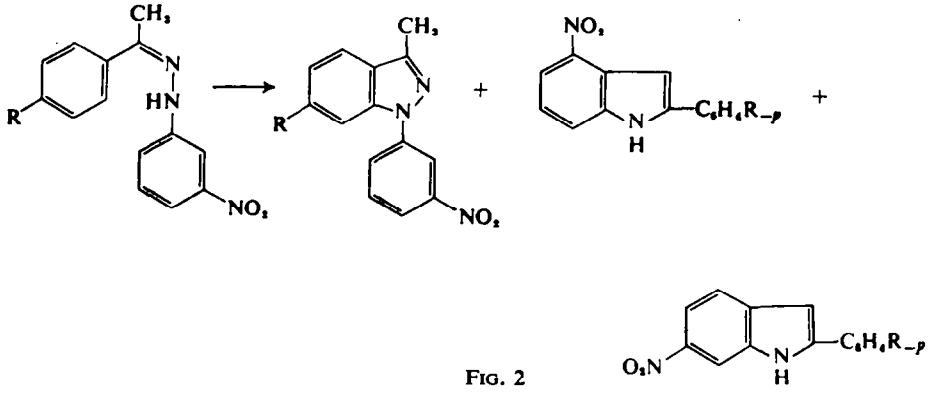


FIG. 2

The increased basicity of the *m*-nitrophenylhydrazones, which will favour a partial protonation at both nitrogen atoms when treated with PPA under the reaction conditions, can be one of the deciding factors in the complex sequence of reactions responsible for the formation of indoles in these cases. The monoprotonated fraction of the hydrazone, in equilibrium with the diprotonated molecules, could originate the indazole, as already discussed. In the case of the *p*-nitrophenylhydrazones, monoprotonation would be so predominant that only indazoles are produced.

The activity of PPA in producing indoles and indazoles from *m*-nitrophenylhydrazones seems to be specific, because they are not formed when the same hydrazones are treated with hydrochloric or sulphuric acids under the usual conditions of the Fischer synthesis.

The failure of stronger acids to produce indoles shows that diprotonation of the hydrazones is not the only factor determining their formation, when PPA is employed. Evidently the use of PPA must favour other steps of the reaction, e.g. the imino-enamine tautomerism. One could speculate that the exclusive formation of indoles when employing the *p*-nitro-, *m*-nitro- or *o*-nitrophenylhydrazones of propiophenone, with a methylene group which tautomerizes easily, results from the displacement of the imino-enamine equilibrium towards this latter structure. In these cases indazoles were never isolated and indoles were produced,[5] not only with PPA but also with the stronger acids.

[4] G. Berti, A. Da Settimo and G. Segnini, *Gazz. Chim. Ital.* **90**, 539 (1960).

[5] A. R. Frasca, *Anal. Assoc. Quim. Argentina* **50**, 162 (1962).

TABLE 5. NEW NITROPHENYLHYDRAZONES FROM ACETOPHENONES

(a) p-*Nitrophenylhydrazones from substituted acetophenones*

Substituent	m.p.	N_{found}	$N_{req.}$	Substituent	m.p.	N_{found}	$N_{req.}$
4-Br	242–243°	12·23	12·57	2-NO_2	214–215°	18·40	18·66
3-OH	189–190°	15·35	15·49	4-OAc	208–209°	13·52	13·42
4-OH	184–185°	15·00	15·49	2,4-di-Me	152–153°	15·25	14·83
4-Et	197–198°	14·72	14·83	2,4-di-OMe	156–157°	13·46	13·33
4-OEt	203–204°	13·96	14·04	2,5-di-OMe	157–158°	13·06	13·33
4-Ph	194–195°	12·43	12·69	2,4,5-tri-Me	138–140°	14·50	14·13

(b) m-*Nitrophenylhydrazones from substituted acetophenones*

Substituent	m.p.	N_{found}	$N_{req.}$	Substituent	m.p.	N_{found}	$N_{req.}$
H	163–164°	16·60	16·46	4-OMe	167–168°	14·46	14·73
4-Cl	192–193°	14·50	14·50	4-Ph	236–237°	12·79	12·69
4-Me	168–169°	15·63	15·60	2,4-di-Me	121–122°	15·10	14·84

(c) o-*Nitrophenylhydrazones from substituted acetophenones*

Substituent	m.p.	N_{found}	$N_{req.}$	Substituent	m.p.	N_{found}	$N_{req.}$
H	138–139°	16·26	16·46	4-Me	132–133°	15·35	15·60
4-Cl	157–158°	14·20	14·50	4-OMe	144–145°	14·55	14·73

EXPERIMENTAL

M.p.s are not corrected. UV spectra (Zeiss RPQ 20 C spectrophotometer using EtOH). NMR spectra (Varian A-60 spectrometer, with TMS as internal standard).

Nitrophenylhydrazones. They were obtained heating equimolecular amounts of the carbonyl compound and the nitrophenylhydrazine in EtOH, with a few drops AcOH. New hydrazones prepared during this work are indicated in Table 5.

General method for the preparation of 1-p-*nitrophenyl-indazoles*

The nitrophenylhydrazones of the corresponding aldehydes and ketones were heated in an oil bath with 10–15 times their wt of PPA. The heating was carried on slowly under continuous stirring, up to 140–165°, as mentioned in Tables 1 and 2, maintaining this temp for 2–5 min. A marked darkening of the mixture was observed. After finishing the heating, the reaction mixture was cooled and diluted with water. The dark suspension was extracted with chf and the organic phase washed with water, dried (Na_2SO_4) and evaporated. The residue obtained was chromatographed on alumina (Woelm, act. III) using benzene as eluent. In all cases the indazole was present in the first yellow fraction which eluted.

1-p-*Nitrophenyl-5,6-dimethoxy-indazole* (XVII) by methylation of XVI

Compound XVI (50 mg) was dissolved in acetone (5 ml) containing K_2CO_3 (100 mg) and heated 2 hr on a water bath with a slight excess of MeI. After evaporating the solvent, crystallization from EtOH gave yellow needles, m.p. 210–211°.

4,4′-*Bis*-1-(3-*methyl-indazole*) *azoxybenzene* (XXXI)

(a) Compound II was dissolved in a N KOH(EtOH-water 9:1) and refluxed 4 hr. During the heating a yellow crystalline product separated, which after cooling was filtered off. Crystallization from benzene yielded yellow needles, m.p. 223–224°. λ_{max} 308 mμ (log ε 3·94); 400 (4·62). (Found C, 73·34; H, 4·84; N, 18·33. $C_{28}H_{22}N_6O$ requires: C, 73·56; H, 4·89; N, 18·45%.) By evaporation of the mother liquids a product separated, which on purification was identified as XX. It could also be obtained reducing the azoxy compound with $SnCl_2$ in a mixture of HCl and AcOH.

(b) The same azoxy compound was obtained heating a solution of the II in EtOH–water (2:1) with KBH_4.

4,4'-Bis-1-(3-methyl-indazole) azobenzene (XXXII)

To a solution of II (110 mg) in anhydrous ether (30 ml), LAH[4] (150 mg) was added and the mixture heated 10 min. After destroying the excess LAH[4] and evaporating the solvent, the product was crystallized from benzene-light petroleum, yielding red prisms, m.p. 220–221°. λ_{max} 241 mμ (log ε 4·07); 392 (4·17). (Found: C, 75·87; H, 5·21; N, 19·01. $C_{28}H_{22}N_6$ requires: C, 76·00; H, 5·01; N, 18·99%.)

Reducing the azo compound with $SnCl_2$ in a mixture of HCl and AcOH, XX was obtained.

Reduction of 1-p-*nitrophenyl-indazoles to* 1-p-*aminophenyl-indazoles*

The indazole (150 mg) was dissolved in AcOH (2 ml) and to the solution HCl (2 ml) was added, together with $SnCl_2$ (850 mg). The mixture was heated 20 min, cooled and after dilution with water made alkaline with K_2CO_3, extracting with ether, which was washed with water, dried (Na_2SO_4) and evaporated. Crystallization solvents are indicated in Table 3.

Oxidation of the 1-p-*aminophenyl-indazoles*

3-*Methyl-indazole* (XXXIII). To a solution of the amine (110 mg) in cooled 25% H_2SO_4 (2 ml), $Na_2Cr_2O_7$ (50 mg) dissolved in water (0·5 ml) was added slowly. After 2 hr at 0° the mixture was diluted with water and distilled with steam. Extraction of the distillation liquids with chf yielded *p*-quinone, identified through its semicarbazone, IR spectrum and mixed m.p. The mother liquids of the oxidation were alkalinized with 10% NaOH and extracted with ether. The etheral phase was washed with water and dried (Na_2SO_4). After evaporation colourless needles were obtained from water, m.p. 110–111°, (60%) λ_{max} 255 mμ (log ε 3·42); 290 (3·58). (Found: 72·50; H, 6·14; N, 21·78. Calc. for $C_8H_8N_2$: C, 72·69; H, 6·11; N, 21·20%.) This substance was identified with 3-methylindazole prepared by the method of Fischer and Tafel,[5] through its mixed m.p., UV and IR spectra and preparation of its picrate, yellow needles from EtOH, m.p. 198–199°. (Auwers[6] gave m.p. 198·5–199·5°).

Indoles and indazoles obtained by treatment of m-*nitrophenyl-hydrazones with PPA*

(a) *From acetophenone* m-*nitrophenylhydrazone.* Following the general technique indicated for the indazoles, the hydrazone was heated with PPA to 155°. During the chromatography on alumina the formation of two coloured bands was observed, which separated neatly using benzene as eluent.

1-m-*Nitrophenyl-3-methyl-indazole.* From the elution fraction containing the first coloured band, yellow needles m.p. 129–130° (8%) were obtained after crystallization from EtOH–water. λ_{max} 253 mμ (log ε 4·41), 305 (4·08). (Found: 66·28; H, 4·39; N, 16·71. $C_{14}H_{11}H_3O_2$ requires: C 66·39; H, 4·38; N, 16·59%.)

2-*Phenyl-4-nitroindole.* Crystallization from EtOH–water of the product obtained from the second coloured band yielded red prisms, m.p. 201–202° (2%), λ_{max} 230 mμ (log ε 4·24), 275 (4·19), 405 (4·00). (Found: C, 70·31; H, 4·40; N, 11·46. $C_{14}H_{10}N_2O_2$ requires: C, 70·57; H, 4·24; N, 11·76%.)

(b) *From* p-*chloroacetophenone* m-*nitrophenylhydrazone*—1-m-*Nitrophenyl-3-methyl-6-chloro-indazole.* Yellow needles from EtOH, m.p. 136–137° (7%), λ_{max} 256 mμ (log ε 4·50), 306 (4·00). (Found: C, 58·34; H, 3·75; N, 14·50; Cl, 12·50. $C_{14}H_{10}ClN_3O_2$ requires: C, 58·44; H, 3·62; N, 14·60; Cl, 12·32%.)

2-p-*Chlorophenyl-4-nitroindole.* Orange prisms from EtOH–water, m.p. 190–191° (10%), λ_{max} 274 mμ (log ε 4·10), 405 (3·85). (Found: C, 62·02; H, 3·52; Cl, 12·50; N, 10·05. $C_{14}H_9ClN_2O_2$ requires: C, 61·66; H, 3·34; Cl: 13·00; N, 10·27%.)

2-p-*Chlorophenyl-6-nitroindole.* Yellow prisms from EtOH–water, m.p. 260–261° (5%), λ_{max} 254 mμ (log ε 4·20), 382 (4·00). (Found: C, 61.87; H, 3·40; Cl, 12·78; N, 9·95. $C_{14}H_9ClN_2O_2$ requires: C, 61·66; H, 3·34; Cl, 13·00; N, 10·27%.)

(c) *From* p-*methylacetophenone* m-*nitrophenylhydrazone*—1-m-*Nitrophenyl-3,6-dimethylindazole.* Yellow needles from EtOH, m.p. 122–123° (5%), λ_{max} 215 mμ (log ε 4·28), 258 (4·36), 306 (4·06). (Found: C, 67·64; H, 5·14; N, 15·51. $C_{15}H_{13}N_3O_2$ requires: C, 67·41; H, 4·90; N, 15·72%.)

[6] K. v. Auwers, *Ber. Dtsch. Chem. Ges.* **52**, 1338 (1919).

2-p-*Methylphenyl-4-nitroindole*. Red-orange prisms from EtOH, m.p. 215 (3%), λ_{max} 216 mμ (log ε 4·18); 277 (4·20), 411 (3·98). (Found: C, 71·45; H, 4·97; N, 11·26. $C_{15}H_{12}N_2O_2$ requires: C, 71·42; H, 4·80; N, 11·10%.)

2-p-*Methylphenyl-6-nitroindole*. Red prisms from EtOH, m.p. 193–194° (3%), λ_{max} 217 mμ (4·20), 258 (4·22), 394 (4·20). (Found: C, 71·25; H, 5·00; N, 10·96. $C_{15}H_{12}N_2O_2$ requires: C, 71·42; H, 4·80; N, 11·10%.)

(d) *From* p-*methoxyacetophenone* m-*nitrophenylhydrazone*—1-m-*Nitrophenyl-3-methyl-6-methoxyindazole*. Yellow needles from EtOH, m.p. 153–154° (10%), λ_{max} 260 mμ (log ε 4·44), 292 sh (4·01). (Found: C, 63·78; H, 4·56; N, 15·00. $C_{15}H_{13}N_3O_3$ requires: C, 63·60; H, 4·63; N, 15·83%.)

(e) *From* p-*phenylacetophenone* m-*nitrophenylhydrazone*—1-m-*Nitrophenyl-3-methyl-6-phenylindazole*. Yellow needles from EtOH, m.p. 150–151° (15%), λ_{max}245 mμ (log ε 4·48), 263 (4·48), 311 sh (3·98). (Found: C, 72·44; H, 4·77; N, 12·74. $C_{20}H_{15}N_3O_2$ requires: C, 72·93; H, 4·59; N, 12·76%.)

(f) *From* 2,4-*dimethylacetophenone* m-*nitrophenylhydrazone*—1-m-*Nitrophenyl-3,4,6-trimethylindazole*. Yellow prisms from EtOH, m.p. 128–129° (4%), λ_{max} 274 mμ (log ε 4·31). (Found: C, 68·17; H, 5·75; N, 14·45. $C_{16}H_{15}N_3O_2$ requires: C, 68·31; H, 5·37; N, 14·94%.)

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