Reactivity of 1,1-Disubstituted Indazol-3-ylio Oxides: Synthesis of some Substituted Indazolols and Indazolinones

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Some aspects of the reactivity of 1,1-disubstituted indazol-3-ylio oxides (indazolol-derived aminimides) have been studied. Treatment of these compounds with hydrochloric acid gave the corresponding indazolium salts which, through elimination of an alkyl chloride, afforded 1-substituted indazol-3-ols. Treatment with alkoxides yielded *N'*,*N'*-disubstituted 2-alkoxybenzohydrazides or 1-substituted indazolols (aryl or alkyl ether elimination products, respectively). The thermal rearrangements of indazolylio oxides gave 1-substituted indazolols, 1,2-disubstituted indazolinones and 3-alkoxy-1-alkylindazoles depending on the substituents. The direct cyclization of *N'*,*N'*-disubstituted 2-chloro-5-nitrobenzohydrazides to indazole derivatives as well as the reactivity of some of the above mentioned compounds are also reported.

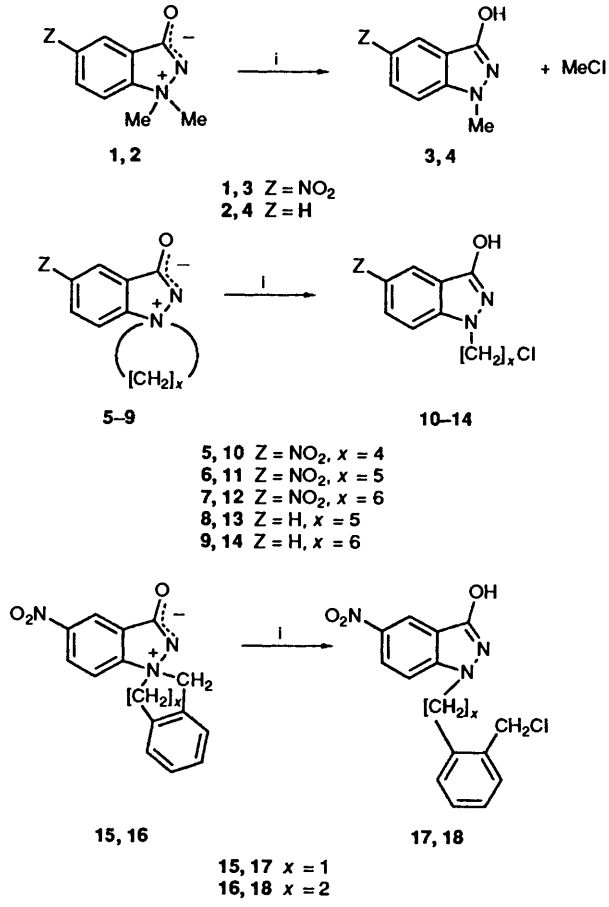
We have recently obtained[1,2] a series of previously unknown indazol-3-ylio oxides (**1**,**2**, **5**–**9**, **15** and **16**) by cyclization of some readily available *N'*,*N'*-disubstituted 2-halogenobenzohydrazides. Indazolylio oxides are, in fact, indazolol-derived aminimides, and according to the reactivity[3] found in other compounds of this class, especially in some aminimides derived from pyrazol-3-one[4–6] and benzothiadiazole 1,1-dioxide,[7] we expect these products to be valuable intermediates in the synthesis of differently substituted indazolols and indazolinones.[1]

Results and Discussion

The reactivity of compounds **1**, **2**, **5**–**9**, **15** and **16** is related, in general, with that of the above mentioned pyrazole- and benzothiadiazole-derived aminimides;[4–7] nevertheless, some unique reactions have also been found to occur in our compounds. In both cases, the reactivity of indazolylio oxides seems to be somewhat dependent on the existence, or otherwise, of the nitro group at position 5 of the indazole ring and on the nature of the substituents linked to the quaternary nitrogen atom.

Indazolylio oxides **1**, **2**, **5**–**9**, **15** and **16**, when refluxed with 6 mol dm^{-3} hydrochloric acid, underwent elimination of an alkyl chloride; 1,1-dimethyl derivatives **1** and **2** afforded, respectively, the corresponding 1-methylindazolols **3** and **4**, and the other betaines gave chloroalkyl compounds **10**–**14**, **17** and **18** (Scheme 1, Tables 1 and 2). In the case of tetrahydroisoquinoline-derived betaine **16**, although two reaction products could be formed, only that resulting from a 'benzyl chloride' elimination (**18**) was detected. A similar behaviour of indazolylio oxides has been observed with hydrobromic and hydroiodic acids, and thus 5-bromo and 5-iodo analogues of compound **11** were obtained from betaine **6** and the corresponding hydrohalic acids. Related 1-(ω-hydroxyalkyl)indazolols have usually been detected as minor by-products (TLC) in these reactions; nevertheless, only compound **19**, arising from homopiperidine-derived betaine **7**, was isolated and characterized.

At room temperature, the most reactive betaines upon reaction with 6 mol dm^{-3} hydrochloric acid were those derived from pyrrolidine **5**, isoindoline **15** and tetrahydroisoquinoline **16**, in which decomposition started almost immediately, followed, in decreasing reactivity order, by those derived from dimethylamine **1** and homopiperidine **7**. Under these conditions, dimethylamine and piperidine derivatives **2** and **6** showed only minor decomposition after a week, and betaines **8** and **9** did not react at all.



Scheme 1 *Reagents and conditions:* i, aq. HCl, reflux

These reactions, which can be related to the thermal decomposition of trialkylanilinium halides,[8,9] have been found to take place through the intermediate indazolinium salts; however, and according to the aforementioned reactivity of indazolylio oxides with hydrochloric acid, most of our compounds decomposed, even at room temperature, following the aforementioned pattern, and only chlorides **20**–**23** were stable enough to be isolated and characterized. These salts

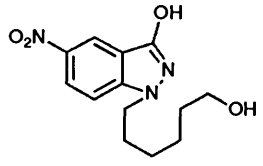
also decomposed, however, at the melting point, yielding, respectively, the corresponding alkyl chloride elimination derivatives **11**, **4**, **13** and **14** as initial products. Although 6-chlorohexyl derivative **14** was stable under these conditions, 5-chloropentyl derivatives **11** and **13** underwent further cyclization to the corresponding diazepinoindazolones **25** and **26** (see below). In the case of salt **21**, 1-methylindazol-3-ol **4** was the major product; nevertheless, 1,2-dimethylindazolin-3-one and 3-methoxy-1-methylindazole, probably formed by the action of the evolved methyl chloride on the indazolol **4**, could also be identified among the thermolysis products.

1-(ω-Chloroalkyl)indazolols **10**, **11**, **13**, **17** and **18** could easily be cyclized to the corresponding condensed indazolinones **24**–**28** by treatment with potassium carbonate in refluxing acetone (Table 3, method A). However, under the same conditions 1-(6-chlorohexyl)indazolols **12** and **14** did not undergo this intramolecular nucleophilic substitution–cyclization.

Table 1 M.p.s and yields (from indazolylio oxides and hydrochloric acid) of 1-substituted indazolols **3**, **4**, **10**–**14**, **17** and **18**

Compound	Yield (%) (starting indazolylio oxide)	M.p. (°C) (solvent)
3	96 (**1**)	281–283 (PrOH)[a]
4	72 (**2**)	151–153 (Pr^{i}OH)[b]
10	92 (**5**)	179–181 (decomp.) (Pr^{i}OH)
11[c]	87 (**6**)	200–202 (decomp.)[d] (Pr^{i}OH)
12	88 (**7**)	171–173 (Pr^{i}OH)
13	70[e] (**8**)	89–91 (PrOH)
14	75 (**9**)	75–77 (PrOH)
17	86 (**15**)	174–176 (decomp.) (Pr^{i}OH)
18	89 (**16**)	177–178 (decomp.) (Pr^{i}OH)

[a] M.p. 285–286 °C (ref. 10). [b] M.p. 153 °C (ref. 11). [c] Bromo analogue: 80% yield, m.p. 176–178 °C (decomp.) (from toluene); iodo analogue: 59% yield, m.p. 160–163 °C (decomp.) (from toluene). [d] M.p. 184–186 °C (ref. 12). [e] Condensed indazolone **26** (10% yield) was also obtained.



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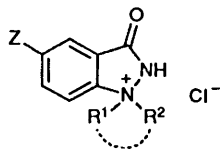
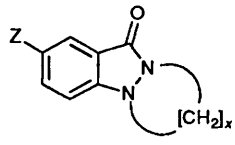
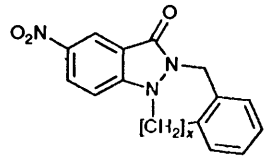


20 Z = NO_2, R^1·····R^2 = $[CH_2]_5$
21 Z = H, R^1 = R^2 = Me
22 Z = H, R^1·····R^2 = $[CH_2]_5$
23 Z = H, R^1·····R^2 = $[CH_2]_6$



24 Z = NO_2, *x* = 4
25 Z = NO_2, *x* = 5
26 Z = H, *x* = 5



27 *x* = 1
28 *x* = 2

Indazolylio oxides were also decomposed by some other nucleophilic agents such as alkoxides; their behaviour towards potassium carbonate was similar, but the decompositions were slower than those with alkoxides. In the few cases we have

Table 2 ^{1}H NMR spectra (δ_H) of 1-substituted indazolols **3**, **4**, **10**–**14**, **17**–**19**, **32**, **38** and **39**

Compound (solvent)	NCH_n[a]	XCH_2[a]	Other signals of side-chain
3[b]	3.88		
[$(CD_3)_2SO$]	(3 H, s)		
4	3.83		
($CDCl_3$)	(3 H, s)		
10	4.25	3.60	2.2–1.5
[$(CD_3)_2SO$]	(2 H, t)	(2 H, t, $ClCH_2$)	(4 H, m, $C[CH_2]_2C$)
11[c]	4.27	3.54	2.00, 1.85 and 1.55
($CDCl_3$)	(2 H, t)	(2 H, t, $ClCH_2$)	(all 2 H, all m, $C[CH_2]_3C$)
12	4.26	3.51	2.2–1.1
($CDCl_3$)	(2 H, t)	(2 H, t, $ClCH_2$)	(8 H, m, $C[CH_2]_4C$)
13[d]	4.19	3.50	1.93, 1.82 and 1.48
($CDCl_3$)	(2 H, t)	(2 H, t, $ClCH_2$)	(all 2 H, all m, $C[CH_2]_3C$)
14	4.18	3.49	1.90, 1.75, 1.48 and 1.35
($CDCl_3$)	(2 H, t)	(2 H, t, $ClCH_2$)	(all 2 H, all m, $C[CH_2]_4C$)
17	5.66	4.96	7.6–6.8
[$(CD_3)_2SO$]	(2 H, s)	(2 H, s, $ClCH_2$)	(4 H, m, ArH)
18	4.50	4.75	3.21 (2 H, t, CH_2CH_2Ar)
[$(CD_3)_2SO$]	(2 H, t)	(2 H, s, $ClCH_2$)	and 7.33 (1 H) and 7.13 (3 H) (both m, ArH)
19	4.21	3.33	1.76 (2 H) and 1.26 (6 H)
[$(CD_3)_2SO$]	(2 H, t)	(2 H, t, OCH_2)	(both m, $C[CH_2]_4C$)
32	4.17	3.33	1.90 (2 H) and 1.50 (6 H)
($CDCl_3$)	(2 H, t)	(4 H, m, CH_2OCH_2)	(both m, $C[CH_2]_3C$ and CH_2Me) and 0.87 (3 H, t, Me)
38[e]	4.25		2.12, 1.95 and 1.44
($CDCl_3$)	(2 H, t)		(all 2 H, all m, $C[CH_2]_3C$)[f]
39	4.11		2.00, 1.81 and 1.35
($CDCl_3$)	(2 H, t)		(all 2 H, all m, $C[CH_2]_3C$)[g]

[a] The value of coupling constants in NCH_2 and XCH_2 triplets is ~6 Hz. [b] Indazole ring: 8.68 (1 H, d, J_m 3, 4-H), 8.17 (1 H, dd, J_m 3, J_o 9, 6-H) and 7.60 (1 H, d, J_o 9, 7-H). [c] Br analogue ($CDCl_3$): 4.27 (2 H, t, NCH_2), 3.41 (2 H, t, $BrCH_2$) and 1.96 (4 H) and 1.51 (2 H) (both m, $C[CH_2]_3C$); I analogue: 4.26 (2 H, t, NCH_2), 3.17 (2 H, t, ICH_2) and 1.97, 1.88 and 1.46 (all 2 H, all m, $C[CH_2]_3C$). [d] Indazole ring: 7.78 (1 H, d, J_o 8, 4-H), 7.42 (1 H, m, 6-H), 7.25 (1 H, d, J_o 8, 7-H) and 7.08 (1 H, m, 5-H). [e] Indazole ring: 8.78 (1 H, d, J_m 3, 4-H), 8.29 (1 H, dd, J_m 3, J_o 9, 6-H) and 7.28 (1 H, d, J_o 9, 7-H). [f] Vinyl group: 5.77 (1 H, m, J_{trans} 17, J_{cis} 10, 5'-H), 5.02 (1 H, m, 6'-H_{trans}) and 4.96 (1 H, m, 6'-H_{cis}). [g] Vinyl group: 5.73 (1 H, m, J_{trans} 17, J_{cis} 10, 5'-H), 4.95 (1 H, m, 6'-H_{trans}) and 4.89 (1 H, m, 6'-H_{cis}).

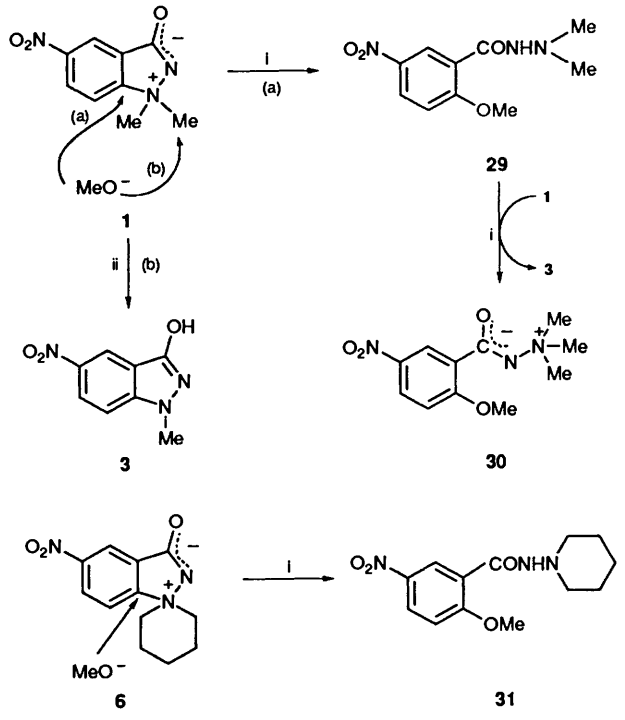
Table 3 M.p.s and yields of 1,2-disubstituted indazolinone **34** and condensed indazolinones **24–28** and **46**

Compound	Yield (%) (starting material; method)	M.p. (°C) (solvent)
24	95 (**10**; A) 46[a] (**5**; B) 91 (**41**; C)	204–206 (PrOH)
25	96 (**11**; A) 33[c] (**6**; B) 60[d] (**42**; C)	158–160[b] (PrOH)
26	98 (**13**; A) *e* (**8**; B)	96–98 (hexane–C_6H_6)
27	97 (**17**; A) 83 (**15**; B) 97 (**44**; C)	212–214 (acetone)
28	98 (**18**; A) 95 (**16**; B) 73 (**45**; C)	198–200 (acetone)
34	18[f] (**1**; B) *h* (**40**; C)	179–181[g] (toluene)
46	*i* (**16**; B) 12 (**45**; C)	185–187 (Pr^iOH)

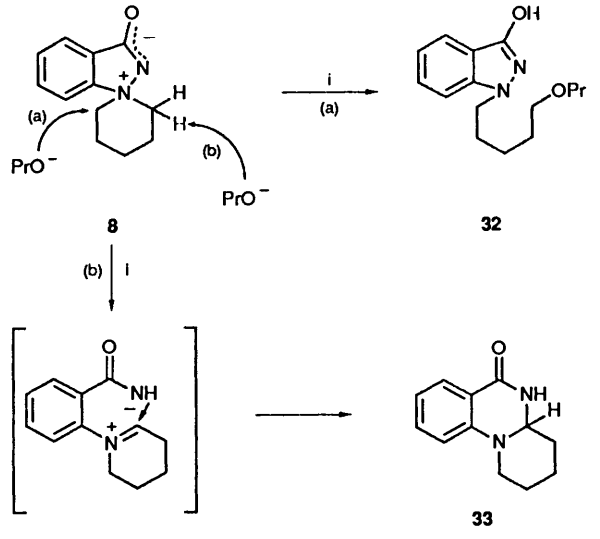
[a] Macrocyclic derivative **36** (23% yield) was also formed. [b] M.p. 157–159 °C (ref. 12). [c] Macrocyclic derivative **37** (40% yield) was also formed. [d] 1-(Chloroalkyl)indazolol **11** (20% yield) was also formed. [e] Very complex reaction mixture; compound **26** could only be tentatively detected by TLC. [f] 3-Methoxy-1-methyl-5-nitroindazole **35** (72% yield) and 1-methyl-5-nitroindazolol **3** (7% yield) were also formed. [g] M.p. 182 °C (ref. 13). [h] Only 1-methyl-5-nitroindazolol **3** (98% yield) was formed. [i] Only the isomeric compound **28** was formed in the Wawzonek rearrangement of indazolylio oxide **16**.

studied, we have been able to detect cleavage of N^+–R, N^+–Ar and N^+–N^- bonds depending on the substituents. Related competitive decomposition patterns (cleavage of N^+–aryl *vs.* N^+–alkyl bonds) have been observed in the reaction of trialkylanilinium salts with alkoxides.[8,9] Nitro derivatives **1** and **6**, treated with sodium methoxide in refluxing methanol, afforded as major products the corresponding *N'*,*N'*-disubstituted 2-methoxybenzohydrazides **29** and **31**, arising from removal of the aryl group linked to the quaternary nitrogen atom. In the case of dimethyl derivative **1**, 1-methyl-5-nitroindazolol **3** and the open-chain aminimide **30** could also be isolated as by-products. Bearing in mind the alkylating power of indazolylio oxides,[2] aminimide **30** must be derived from hydrazide **29** and betaine **1**; nitroindazolol **3** can proceed, of course, from this alkylation reaction or, as commented on below, from elimination of dimethyl ether (Scheme 2). On the other hand, betaines **2** and **8**, without a nitro group in the indazole ring, required sodium propoxide in refluxing propan-1-ol for an efficient transformation, and gave, as major products, the corresponding dialkyl ether-elimination derivatives arising from removal of one of the alkyl groups linked to the quaternary nitrogen atom (Scheme 3). Following this procedure, compound **2** gave 1-methylindazolol **4**, and the piperidine derivative **8** afforded 1-(5-propoxypentyl)indazolol **32** together with a by-product which was shown to be the pyridoquinazoline **33**. This compound can be derived from the corresponding betaine through a base-catalysed indazole ring opening, similar to that proposed by Martin *et al.*[7] to explain related processes in benzothiadiazole-derived betaines. An alternative mechanism based on the rearrangement of an intermediate nitrene[7] seems unlikely to occur under our conditions.

Indazolol-derived aminimides underwent rearrangements when heated in nitrobenzene at ~200 °C (Scheme 4). The reactivity and the thermolysis patterns of these compounds were in each case also dependent on the nature of the substituents. Some of the decomposition pathways observed in our compounds (*N*,*N*-[3,4] and *N*,*O*-alkyl shifts,[4–6] and alkene elimination[3,7]) have also been found to occur in other



Scheme 2 *Reagents:* i, MeO^-; ii, MeO^- or **29**

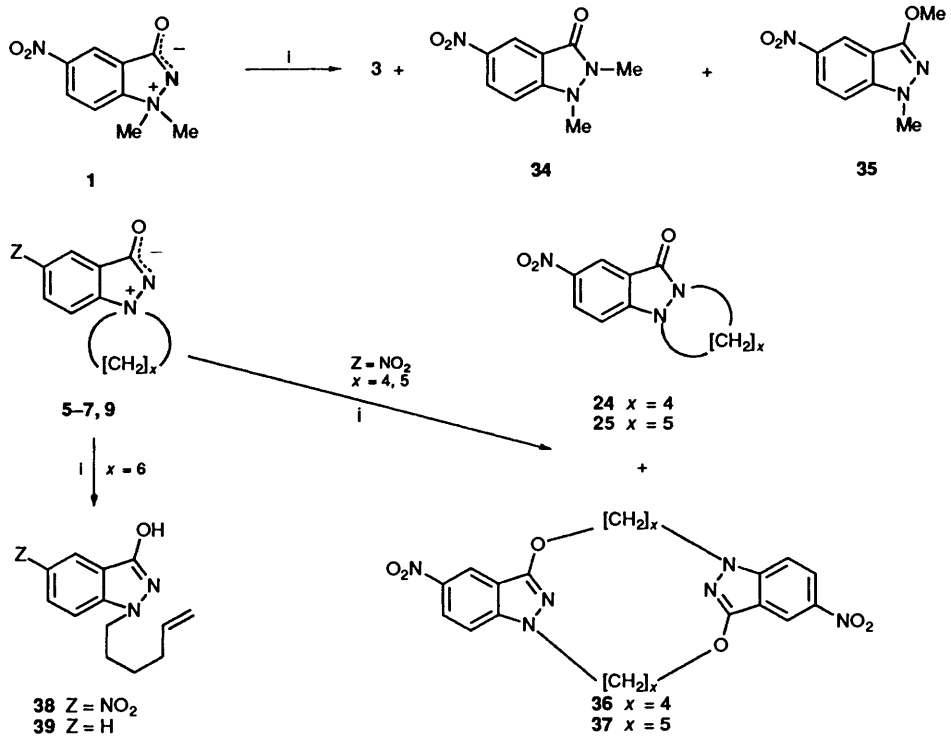


Scheme 3 *Reagents:* i, Pro^-

aminimides. However, we have not been able to detect products arising from N^+–N^- bond cleavage; this process, leading initially to highly reactive nitrenes, is not unusual in related open-chain[3] and benzothiadiazole-derived[7] aminimides. On the other hand, we have observed that the decompositions of nitro derivatives **1**, **5–7**, **15** and **16** are usually easier and cleaner than those of indazolylio oxides without an NO_2 group.

Under the described thermolysis conditions, dimethyl derivative **1** gave a mixture of 1,2-dimethyl-5-nitroindazolinone **34** (Wawzonek rearrangement product) (Table 3, method B) and 3-methoxy-1-methyl-5-nitroindazole **35**; traces of the corresponding 1-methylindazolol **3** were also formed.

Betaines **5**, **6**, **15** and **16**, in which the *N*,*N*-alkyl shift (Wawzonek rearrangement) leads to new 6- or 7-membered rings, easily gave the corresponding condensed indazolinones **24**, **25**, **27** and **28** (Table 3, method B); only the product arising from the rearrangement of the 'benzyl group' **28** was produced



Scheme 4 *Conditions:* i, nitrobenzene, reflux

in the thermolysis of tetrahydroisoquinoline-derived betaine **16**. In the case of pyrrolidine and piperidine derivatives **5** and **6**, *N*,*O*-alkyl-shift products were also detected. Nevertheless, it seems that the polymethylene chain of these compounds is too short to allow the formation of an intramolecular rearrangement product, and thus only the dimeric macrocyclic derivatives **36** and **37**, resulting from two intermolecular *N*,*O*-alkyl shifts, were observed.

Homopiperidine-derived betaines **7** and **9** reacted following a different pattern, yielding the corresponding alkene elimination products **38** and **39**.

Compounds **2** and **8**, without a nitro group in the indazole ring, reacted very slowly and yielded complex reaction mixtures. Although some of the expected thermolysis products were tentatively identified by TLC, we could isolate only 3-methoxy-1-methyl-1*H*-indazole arising from betaine **2**.

Finally, and according to our preliminary reports[1,12] on the thermal cyclization of the 2-chloro-5-nitrobenzohydrazide **42**, we have found that *N*′,*N*′-disubstituted 2-chlorobenzohydrazides **40–45**, heated at the melting point, or (better) in nitrobenzene at 200 °C, undergo cyclization to give indazole derivatives in good yield (Schemes 5 and 6). From the obtained compounds we believe that the initially formed products must be the corresponding indazolinium chlorides which, as commented above, are unstable and decompose, through elimination of an alkyl chloride, to give the corresponding 1-alkylindazolols. Under the reaction conditions 1-methyl-5-nitroindazolol **3** and 1-(6-chlorohexyl)-5-nitroindazolol **12** were stable compound which could easily be isolated; the other ω-chloroalkyl derivatives were, however, unstable and underwent further cyclization, slowly in the case of chloropentyl derivative **11**, to the corresponding condensed indazolinones **24**, **25**, **27** and **28** (Table 3, method C). The same behaviour was observed when independently prepared, pure samples of 1-substituted nitroindazolols **3**, **10–12**, **17** and **18** were heated in nitrobenzene at 200 °C. In the thermolysis of *N*-tetrahydroisoquinoline-derived amide **45** we were able to isolate the two isomeric indazolobenzodiazepines **28** and **46** (6:1 ratio), resulting from the two different ring-opening pathways ('benzyl' *vs.* 'phenethyl' chloride elimination) possible in the intermediate indazolinium salt (Scheme 6).

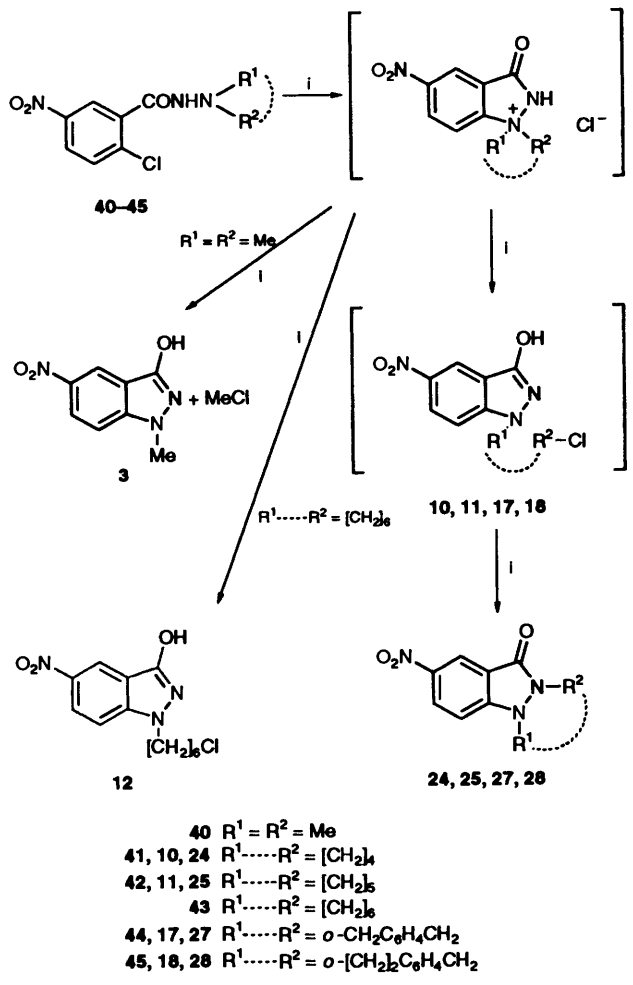
2-Fluoro analogues[1,2] of hydrazides **40–45**, when heated at the melting point, gave very complex reaction mixtures from which, and only in some cases, the corresponding indazolylio oxides could be detected by TLC; under the same conditions, *N*′,*N*′-disubstituted 2-fluoro- and 2-chloro-benzohydrazides[2] (without an NO_2 group in the ring) did not show any decomposition, or else gave only tars.

The spectral data of compounds **3**, **4**, **10–14**, **17–19**, **32**, **38** and **39**, specially the IR[11] and ^{13}C NMR,[14,15] suggested that they are, as depicted in the Schemes, in the usual 3-hydroxy-1*H*-indazole (or 1*H*-indazol-3-ol) tautomeric form. In the mass spectra, the base peaks of indazolols containing a chain of two or more methylene groups linked to N(1) correspond to the 1-indazolylmethyl radical ion (*m*/*z* 192 in 5-nitro derivatives and *m*/*z* 147 in 5-H derivatives). The peak *m*/*z* 192 is present in the spectrum of compound **18**, this result supporting the proposed 1-phenethylindazolol structure of this product, initially based on mechanistic reasons and further confirmed by its cyclization to the condensed indazolinone **28**.

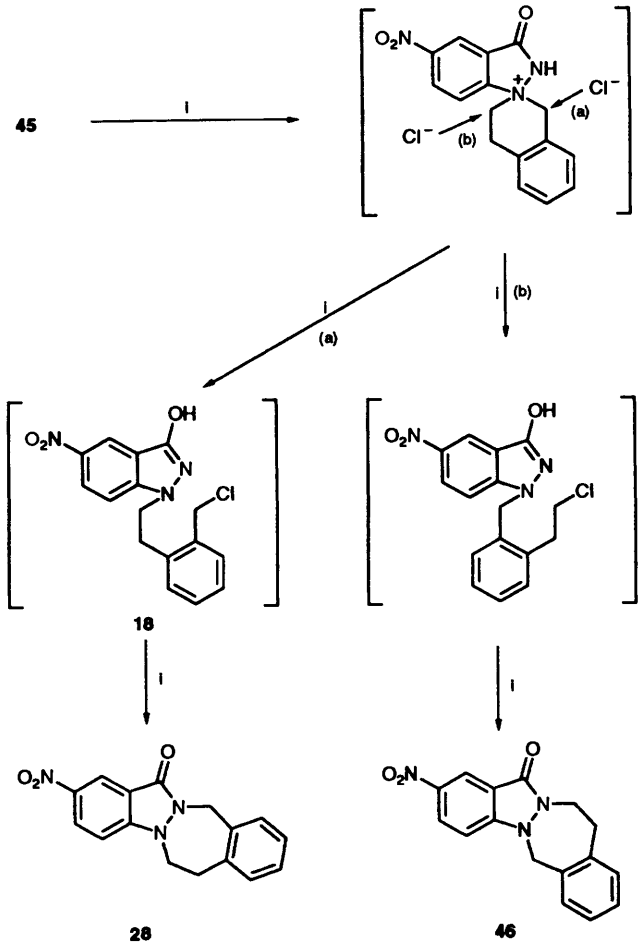
On the other hand an 'indazolinone' structure must be assigned to the indazolinium chlorides **20–23** according to the IR spectral data. The ^1H NMR spectra of these salts are similar to those of the corresponding indazolylio oxides,[1,2] and in the spiro compounds 20, 22 and 23 the protons of the NCH_2 groups are anisochronic.

NMR spectra of *N*′,*N*′-disubstituted 2-methoxybenzohydrazides **29** and **31** show that these compounds appear in solution as mixtures of *Z* and *E* rotamers; the features of this rotamerism are similar to those previously found[2] in related *N*′,*N*′-disubstituted 2-halogenobenzohydrazides. On the other hand, and according to previous reports,[16] only the rotamer in which N^+ and O^- atoms are in the electrostatically stabilized *cis* conformation has been detected in the ^1H NMR spectrum of aminimide **30**.

The dimeric structure of compounds **36** and **37** is supported by their mass spectra. The IR data of these products (C=O stretching band[11] was not present) can only be explained by



Scheme 5 *Conditions:* i, nitrobenzene, reflux



Scheme 6 *Conditions:* i, nitrobenzene, reflux

considering the depicted double N(1)–O linkage between both indazole rings.

Experimental

M.p.s were determined in a Gallenkamp capillary apparatus, and are uncorrected. IR spectra were obtained with a Shimadzu IR-435 spectrophotometer. ^1H (200 or 300 MHz) and ^{13}C NMR (50 or 75 MHz) spectra were recorded on a Varian Gemini-200 or on a Varian XL-300 spectrometer using the signal of the solvent or 1,4-dioxane (for ^{13}C NMR spectra in D_2O) as reference. *J* Values are given in Hz. Mass spectra (electron impact) were obtained at 70 eV on a VG 12-250 (VG Masslab) spectrometer. DC-Alufolien silica gel 60 PF_{254} (Merck, layer thickness 0.2 mm) and silica gel 60 PF_{254} (Merck, 20 × 20 cm plates, layer thickness 2 mm) were used respectively for TLC and preparative TLC (PLC). Flash column chromatography was performed on silica gel 60 (Merck, particle size 0.040–0.063 mm). Microanalyses were performed by the Departamento de Análisis, Centro Nacional de Química Orgánica, C.S.I.C., Madrid, Spain. Since several compounds reported here could be obtained following different procedures, their physical and spectral data, apart from those included in Tables 1–4, are collected at the end of this section.

Reactivity of Indazolylio Oxides **1**, **2**, **5–9**, **15** *and* **16**.—(a) *Treatment with refluxing hydrochloric acid. Preparation of* 1-*substituted indazolols* **3**, **4**, **10–14**, **17** *and* **18**. *General method.* A mixture of an indazolylio oxide (5 mmol) and 6 mol dm^{-3} hydrochloric acid (50 cm^3) was refluxed until the starting material was consumed (TLC, 1 h to 6 days). After addition of water (300 cm^3), the reaction mixture was extracted several times with ethyl acetate or chloroform, to yield the crude indazolols. 1-Methyl derivatives **3** and **4** were chromatographically pure compounds, but halogenoalkyl derivatives **10–14**, **17** and **18**, containing traces of a by-product which could not be separated by recrystallization, were purified by flash column chromatography (chloroform–methanol mixtures). Only in the case of 6-chlorohexyl derivative **12** was the corresponding by-product, which was shown to be the 6-hydroxyhexyl derivative **19**, also isolated (3% yield) from the column.

Compound **8** required a long period of reflux (6 days) to be converted into the corresponding ω-chloroalkyl derivative **13**, and the corresponding condensed indazolinone **26** was subsequently formed as by-product. In this case, a further extraction of the initial chloroform solution with dil. aq. sodium hydroxide was needed to separate the acidic indazolols from the indazolinone **26**. Traces of the corresponding 1-(ω-hydroxypentyl)indazolol were removed, as before, by column chromatography.

Bromo and iodo analogues of chloro compound **11** were obtained following the same procedure but with the corresponding hydrohalic acid.

Yields (following this method) and m.p.s of 1-substituted indazolols **3**, **4**, **10–14**, **17** and **18** are gathered in Table 1.

(b) *Preparation of indazolinium chlorides* **20–23**. In the case of salts without an NO_2 group in the indazole ring (**21–23**), a solution of the corresponding indazolylio oxide (**2**, **8** or **9**) in dil. hydrochloric acid was evaporated to dryness at 40 °C, and the residue was recrystallized (85–87% yield). The indazolinium

Table 4 ^{1}H NMR spectra (δ_H, $CDCl_3$) of 1,2-disubstituted indazolinone **34** and condensed indazolinones **24–28** and **46**

Compound	N(1)CH_n[a]	N(2)CH_n[a]	Other signals of side-chains or condensed rests
24[b]	3.66 (2 H, br t, 6-H_2)	3.93 (2 H, br t, 9-H_2)	2.01 (4 H, br s, 7- and 8-H_2)
25	4.16 (4 H, br, s, 6- and 10-H_2)		1.86 (6 H, br s, 7-, 8- and 9-H_2)
26[c]	4.12 (2 H, m, 6-H_2)	3.91 (2 H, m, 10-H_2)	1.85 (4 H) and 1.74 (2 H) (both m, 7-, 8- and 9-H_2)
27	4.81 (2 H, s, 6-H_2)	5.07 (2 H, s, 11-H_2)	7.33 (4 H, s, 7-, 8-, 9- and 10-H)
28	3.90 (2 H, m, 6-H_2)	5.13 (2 H, s, 12-H_2)	3.35 (2 H, m, 7-H_2) and 7.30 (4 H, m, 8-, 9-, 10- and 11-H)
34	3.53 (6 H, s, Me)		
46	4.84 (2 H, s, 6-H_2)	4.22 (2 H, m, 12-H_2)	3.27 (2 H, m, 11-H_2) and 7.34 (4 H, m, 7-, 8-, 9-and 10-H)

[a] Numbering of indazole nitrogen atoms is, for comparative purposes, as in simple derivatives without condensed rings. [b] Indazole ring: 8.70 (1 H, d, J_m 2, 1-H), 8.36 (1 H, dd, J_m 2, J_o 9, 3-H) and 7.25 (1 H, d, J_o 9, 4-H). [c] Indazole ring: 7.85 (1 H, m, J_o 8, J_m 1, J_p 1, 1-H), 7.49 (1 H, m, J_o 8, J_o 7, J_m 1, 3-H and 7.09 (2 H, m, 2- and 4-H).

chloride **20** was prepared by addition of conc. hydrochloric acid to cold, saturated aq. betaine **6**. The separated solid was filtered off, and washed with cold, dil. hydrochloric acid (83% yield). This compound could not be recrystallized without partial decomposition to the corresponding 5-chloropentyl derivative **11**.

(c) *Treatment of indazolylio oxides* **1**, **2**, **6** *and* **8** *with base.* In the case of nitro derivatives **1** and **6**, a solution of 4 mmol of the corresponding betaine (4 mmol) and sodium methoxide (8 mmol) in methanol (30 cm^3) was refluxed until consumption of the starting material (TLC, 5–24 h). The reaction mixture was then evaporated to dryness, and the residue was dissolved in water. In the case of betaine **6**, extraction of this solution with chloroform afforded the chromatographically pure 2-methoxybenzohydrazide **31** (0.98 g, 88%). When betaine **1** was used as starting material, extraction with chloroform gave a mixture of hydrazide **29** (0.65 g, 68%) and open-chain aminimide **30** (61 mg, 6%), which were separated by flash column chromatography [(40:1) chloroform–methanol]; in this case, treatment of the basic aqueous layer with hydrochloric acid, followed by extraction with ethyl acetate, yielded crude 1-methyl-5-nitroindazol-3-ol **3**, which was purified by PLC using (10:1) chloroform–methanol as eluent (123 mg, 16%).

Treatment of betaines **2** and **8** (4 mmol) with sodium propoxide (8 mmol) in refluxing propan-1-ol was carried out following the same procedure, but the reactions required respectively 1 and 6 days of reflux. The solvent was then evaporated off, and the residue, as before, was dissolved in water. In the case of compound **8**, extraction of this solution with diethyl ether afforded crude pyridoquinazolinone **33**, which after purification by PLC using (30:1) chloroform–methanol as developing solvent yielded pure product (73 mg, 9%). In both cases, acidification of the aqueous solution with hydrochloric acid followed by extraction with chloroform yielded, respectively, 1-methylindazol-3-ol **4** (0.51 g, 86%) and 1-(5-propoxypentyl)indazol-3-ol **32** (0.76 g, 72%); an analytical sample of the latter, which was an oil, was prepared by PLC [(20:1) chloroform–methanol].

For comparative purposes, hydrazides **29** and **31** were also prepared in ~90% yield by acylation[2] of the corresponding *N*,*N*-disubstituted hydrazines with 2-methoxy-5-nitrobenzoyl chloride. Compound **31** could also be obtained, in 79% yield, from 2-chloro-5-nitrobenzohydrazide **42** and sodium methoxide in methanol, following the procedure described for the treatment of betaine **6** with the same reagent. Open-chain aminimide **30** could alternatively be prepared in 89% yield from hydrazide **29** and methyl iodide.[2]

(d) *Thermolysis of indazolylio oxides* **1**, **2**, **5–9**, **15** *and* **16**. A suspension of an indazolylio oxide (5 mmol) in nitrobenzene (30 cm^3) was heated at 190–200 °C until consumption of the starting material (1 h for nitro derivatives **1**, **5–7**, **15** and **16**, 4 h for compound **9**, and 3 days for compounds **2** and **8**), and then was evaporated to dryness. The behaviour of each betaine and the subsequent treatment of the resulting reaction mixtures were dependent on the substituents.

Compound **1** afforded a mixture of 3-methoxy-1-methyl-5-nitroindazole **35**, 1,2-dimethyl-5-nitro-1,2-dihydro-3*H*-indazol-3-one **34**, and 1-methyl-5-nitroindazol-3-ol **3** (see yields in Table 3, method B), which were separated, in this order, by flash column chromatography using chloroform and chloroform–methanol mixtures as eluent.

Betaines **5** and **6** yielded, respectively, mixtures of macrocyclic derivatives **36** and **37**, and condensed indazolones **24** and **25** (see yields in Table 3, method B), which were separated in each case, and following the indicated elution order, by flash column chromatography using chloroform–acetone mixtures. Traces of a by-product of low R_f-value could also be isolated from the thermolysis of betaine **6**; although this compound decomposed during purification, the ^{1}H NMR spectrum of the crude product suggests a pyridoquinazolinone structure analogous to that of compound **33**.

Homopiperidine-derived betaines **7** and **9** afforded the corresponding 1-(hex-5-enyl)indazolols **38** and **39**. These acidic compounds were extracted with 1 mol dm^{-3} sodium hydroxide from a solution of the reaction mixture in chloroform. Acidification of the aqueous layer with dil. hydrochloric acid, followed by extraction with chloroform, yielded pure products **38** (1.17 g, 90%) and **39** (0.81 g, 75%).

Isoindoline- and tetrahydroisoquinoline-derived betaines **15** and **16** gave practically pure condensed indazolinones **27** and **28** respectively (see yields in Table 3, method B). Traces of impurities were removed by flash chromatography through a short silica gel column, using a (30:1) chloroform–methanol mixture as eluent.

Finally, betaines **2** and **8** yielded very complex reaction mixtures. In the first case we were, however, able to isolate 3-methoxy-1-methyl-1*H*-indazole; this compound, with a high R_f-value, was easily separated from the mixture by flash column chromatography using chloroform as eluent (0.16 g, 20%; oil whose spectral data were identical with those previously reported).[11,14] Our efforts to isolate pure 1,2-dimethyl-1,2-dihydro-3*H*-indazol-3-one, also present (TLC) in the crude reaction material, were, however, unsuccessful.

Thermolysis of Indazolinium Chlorides **20–23**.—A solid indazolinium chloride (3 mmol) was heated at 190–200 °C for 10 (**21**, **23**) or 30 min (**20**, **22**), and the reaction mixture was dissolved in chloroform. In the case of salts **20** and **22**, the chloroform solution was washed with 0.5 mol dm^{-3} aqueous sodium hydroxide to separate remaining indazolols; traces of other impurities of low R_f-value were removed by flash column chromatography [(40:1) chloroform–methanol], to afford pure diazepinoindazolones **25** (0.59 g, 80%) and **26** (0.55 g, 91%).

In the case of salts **21** and **23**, the obtained indazolols were extracted from the chloroform solution with 0.5 mol dm^{-3}

sodium hydroxide. Acidification of the aqueous layer with dil. hydrochloric acid, followed by extraction with chloroform, yielded pure 1-methylindazol-3-ol **4** (0.29 g, 65%) or crude 1-(6-chlorohexyl)indazol-3-ol **14**, which was separated (0.61 g, 81%) from traces of low-R_f impurities by column chromatography [(40:1) chloroform–methanol]. 1,2-Dimethyl-1,2-dihydro-3*H*-indazol-3-one and 3-methoxy-1-methyl-1*H*-indazole, also present (TLC) in the crude reaction mixture arising from salt **21**, were not isolated.

Cyclization of 1-(ω-*Halogenoalkyl*)*indazolols* **5**, **6**, **8**, **17** *and* **18** *to Condensed Indazolinones* **24**–**28**.—A mixture of an indazolol (1 mmol) and potassium carbonate (0.28 g, 2 mmol) in acetone (30 cm^3) was refluxed for 1–3 days. The reaction mixture was then evaporated to dryness, and the residue was treated with water and extracted with chloroform. The organic layer was washed several times with water to remove traces of unchanged indazolols and, after evaporation of the solvent, pure condensed indazolones **24**–**28** were obtained in almost quantitative yield (Table 3, method A).

Thermolysis of N′,N′-*Disubstituted* 2-*Chloro*-5-*nitrobenzohydrazides* **40**–**45**.—A solution of a hydrazide (5 mmol) in nitrobenzene (25 cm^3) was heated at 190–200 °C until consumption of the starting material (4.5 h to 2 days). During this time the progress of the reaction was monitored by TLC. After evaporation of the solvent, the residue was treated according to the nature of the obtained products.

1-Methyl-5-nitroindazolol **3** (from hydrazide **40**), pyridazino[1,2-*a*]indazolone **24** (from **41**), 1-(6-chlorohexyl)-5-nitroindazol-3-ol **12** (1.41 g, 95% yield from **43**), and indazolo[1,2-*b*]phthalazinone **27** (from **44**) were obtained as almost pure compounds; traces of impurities were removed by column chromatography using chloroform–methanol mixtures as eluent.

N-Aminopiperidine-derived hydrazide **42** gave, after being heated for 2 days, a (1:3) mixture of 1-(5-chloropentyl)-5-nitroindazol-3-ol **11** and the diazepino[1,2-*a*]indazolone **25**, which were separated by extraction with dil. aq. sodium carbonate or sodium hydroxide as previously reported.[12]

N-Aminotetrahydroisoquinoline-derived hydrazide **45** gave a (6:1) mixture of isomeric indazolobenzodiazepines **28** and **46**, which were separated by PLC using a (30:1) chloroform–acetone mixture as developing solvent.

Yields of indazolinones **24**, **25**, **27**, **28** and **46**, as well as those of indazolols **3** and **11** obtained by this method, are included in Table 3 (method C).

1-*Substituted* 1H-*Indazol*-3-*ols*.—Characteristic bands[11] of 1-substituted indazolols [ν_{max}(Nujol)/cm^{-1} ~1620 and 1580 (C=C), and 1550 (C=N)] were found in the IR spectra of these compounds.

1-*Methyl*-5-*nitro*-1H-*indazol*-3-*ol* **3**. δ_C[$(CD_3)_2SO$] 156.25 (C-3), 142.11 (C-7a), 139.63 (C-5), 121.43 (C-6), 118.51 (C-4), 111.25 (C-3a), 109.77 (C-7) and 35.19 (Me); *m*/*z* 193 (M^+, 100%), 163 (24), 147 (47), 104 (13), 92 (15) and 75 (31).

1-(4-*Chlorobutyl*)-5-*nitro*-1H-*indazol*-3-*ol* **10**. [Found: C, 49.1; H, 4.6; Cl, 13.3; N, 15.6. $C_{11}H_{12}ClN_3O_3$ (269.7) requires C, 49.0; H, 4.5; Cl, 13.15; N, 15.6%]; *m*/*z* 271 (M^+ + 2, 5%), 269 (M^+, 15), 234 (30), 233 (25), 192 (100), 146 (39), 76 (18) and 75 (19).

1-(5-*Chloropentyl*)-5-*nitro*-1H-*indazol*-3-*ol* **11**. δ_C[$(CD_3)_2$-SO] 156.39 (C-3), 141.96 (C-7a), 139.75 (C-5), 121.55 (C-6), 118.63 (C-4), 111.23 (C-3a), 109.84 (C-7), 47.67 (NCH_2), 45.22 ($ClCH_2$), and 31.60, 28.37 and 23.50 ($C[CH_2]_3C$); other data for this compound have been previously reported by us.[12]

1-(5-*Bromopentyl*)-5-*nitro*-1H-*indazol*-3-*ol*. [Found: C, 44.0; H, 4.3; Br, 24.2; N, 12.8. $C_{12}H_{14}BrN_3O_3$ (328.2) requires C, 43.9; H, 4.3; Br, 24.35; N, 12.8%]; *m*/*z* 329 (M^+ + 2, 7%), 327 (M^+, 7), 248 (28), 192 (100) and 146 (37).

1-(5-*Iodopentyl*)-5-*nitro*-1H-*indazol*-3-*ol*. [Found: C, 38.2; H, 3.8; N, 11.1. $C_{12}H_{14}IN_3O_3$ (375.2) requires C, 38.4; H, 3.8; N, 11.2%]; δ_C[$(CD_3)_2SO$] 156.58 (C-3), 142.16 (C-7a), 139.95 (C-5), 121.75 (C-6), 118.82 (C-4), 111.45 (C-3a), 110.06 (C-7), 47.85 (NCH_2), 32.61, 28.20 and 27.27 ($C[CH_2]_3C$), and 8.84 (ICH_2); *m*/*z* 375 (M^+, 31%), 248 (72), 247 (78), 218 (10), 192 (100), 146 (52), 128 (16), 91 (11), 89 (15) and 76 (19).

1-(6-*Chlorohexyl*)-5-*nitro*-1H-*indazol*-3-*ol* **12**. [Found: C, 52.7; H, 5.5; Cl, 12.0; N, 14.1. $C_{13}H_{16}ClN_3O_3$ (297.7) requires C, 52.4; H, 5.4; Cl, 11.9; N, 14.1%]; *m*/*z* 299 (M^+ + 2, 10%), 297 (M^+, 26), 262 (27), 192 (100), 179 (15) and 146 (33).

1-(5-*Chloropentyl*)-1H-*indazol*-3-*ol* **13**. [Found: C, 60.1; H, 6.5; Cl, 14.9; N, 11.5. $C_{12}H_{15}ClN_2O$ (238.7) requires C, 60.4; H, 6.3; Cl, 14.85; N, 11.7%]; δ_C($CDCl_3$) 156.24 (C-3), 141.36 (C-7a), 128.41 (C-6), 121.17 (C-4), 119.21 (C-5), 112.34 (C-3a), 108.59 (C-7), 47.82 (NCH_2), 44.54 ($ClCH_2$), and 32.10, 28.75, and 24.10 ($C[CH_2]_3C$); *m*/*z* 240 (M^+ + 2, 5%), 238 (M^+, 16), 203 (7), 147 (100), 134 (6), 130 (5), 119 (6), 105 (8), 85 (9), 83 (9) and 77 (10).

1-(6-*Chlorohexyl*)-1H-*indazol*-3-*ol* **14**. [Found: C, 62.0; H, 6.7; Cl, 13.9; N, 10.9. $C_{13}H_{17}ClN_2O$ (252.75) requires C, 61.8; H, 6.8; Cl, 14.0; N, 11.1%].

1-[2′-(*Chloromethyl*)*benzyl*]-5-*nitro*-1H-*indazol*-3-*ol* **17**. [Found: C, 56.8; H, 4.0; Cl, 11.2; N, 13.1. $C_{15}H_{12}ClN_3O_3$ (317.7) requires C, 56.7; H, 3.8; Cl, 11.2; N, 13.2%]; δ_C[$(CD_3)_2SO$] 156.77 (C-3), 142.40 (C-7a), 140.15 (C-5), 135.87 (s), 135.40 (s), 130.63 (d), 129.14 (d), 128.28 (d) and 128.17 (d) (Ar side-chain), 122.05 (C-6), 118.67 (C-4), 111.85 (C-3a), 109.97 (C-7), 48.74 (NCH_2) and 44.05 ($ClCH_2$); *m*/*z* 319 (M^+ + 2, 7%), 317 (M^+, 20), 282 (15), 281 (50), 280 (31), 235 (11), 234 (16), 141 (25), 140 (39), 139 (75), 138 (100), 104 (73), 103 (53), 78 (23) and 77 (22).

1-[2′-(*Chloromethyl*)*phenethyl*]-5-*nitro*-1H-*indazol*-3-*ol* **18**. [Found: C, 58.1; H, 4.4; Cl, 10.5; N, 12.7. $C_{16}H_{14}ClN_3O_3$ (331.75) requires C, 57.9; H, 4.25; Cl, 10.7; N, 12.7%]; δ_C[$(CD_3)_2SO$] 156.64 (C-3), 142.06 (C-7a), 139.69 (C-5), 137.43 (s), 135.78 (s), 130.56 (d), 130.22 (d), 128.92 (d) and 127.04 (d) (Ar side-chain), 121.41 (C-6), 118.51 (C-4), 111.27 (C-3a), 109.56 (C-7), 48.95 (NCH_2), 44.39 ($ClCH_2$) and 31.62 (CH_2CH_2Ar); *m*/*z* 333 (M^+ + 2, 4%), 331 (M^+, 13), 295 (39), 294 (30), 248 (10), 192 (100), 146 (21), 117 (17) and 104 (26).

1-(6-*Hydroxyhexyl*)-5-*nitro*-1H-*indazol*-3-*ol* **19**. M.p. 180–183 °C (from toluene) [Found: C, 56.1; H, 6.3; N, 15.3. $C_{13}H_{17}N_3O_4$ (279.3) requires C, 55.9; H, 6.1; N, 15.05%]; *m*/*z* 279 (M^+, 16%), 249 (11), 232 (13), 192 (100), 179 (21), 162 (20), 146 (52), 91 (13) and 76 (10).

1-(5-*Propoxypentyl*)-1H-*indazol*-3-*ol* **32**. Oil [Found: C, 68.6; H, 8.6; N, 10.5. $C_{15}H_{22}N_2O_2$ (262.35) requires C, 68.7; H, 8.45; N, 10.7%]; *m*/*z* 262 (M^+, 9%), 202 (13), 201 (20), 148 (13), 147 (100), 134 (28), 118 (12), 105 (32), 92 (17) and 77 (27).

1-(*Hex*-5′-*enyl*)-5-*nitro*-1H-*indazol*-3-*ol* **38**. M.p. 200–203 °C (from toluene) [Found: C, 60.0; H, 5.6; N, 16.2. $C_{13}H_{15}N_3O_3$ (261.3) requires C, 59.8; H, 5.8; N, 16.1%]; δ_C[$(CD_3)_2SO$] 156.38 (C-3), 141.91 (C-7a), 139.69 (C-5), 138.33 (C-5′), 121.49 (C-6), 118.60 (C-4), 114.96 (C-6′), 111.20 (C-3a), 109.72 (C-7), 47.63 (C-1′), and 32.69, 28.56 and 25.32 (C-2′, -3′ and -4′); *m*/*z* 261 (M^+, 16%), 232 (31), 218 (13), 192 (100), 179 (39), 146 (56), 91 (15) and 76 (15).

1-(*Hex*-5′-*enyl*)-1H-*indazol*-3-*ol* **39**. M.p. 84–86 °C (from PrOH) [Found: C, 72.0; H, 7.4; N, 12.7. $C_{13}H_{16}N_2O$ (216.3) requires C, 72.2; H, 7.5; N, 12.95%]; δ_C($CDCl_3$) 156.09 (C-3), 141.16 (C-7a), 138.20 (C-5′), 128.22 (C-6), 121.10 (C-4), 119.00 (C-5), 114.78 (C-6′), 112.22 (C-3a), 108.58 (C-7), 47.90 (C-1′) and 33.20, 28.94 and 25.97 (C-2′, -3′ and -4′); *m*/*z* 216 (M^+, 19%), 187 (17), 147 (100), 146 (10), 134 (52), 130 (11), 105 (18), 92 (17), 77 (24) and 76 (12).

1,1-*Disubstituted* 3-*Oxoindazolinium Chlorides*.—A characteristic band [ν_{max}(Nujol)/cm^{-1} ~1730 (CO)] was found in the IR spectra of these compounds.

5-*Nitro*-3-*oxo*-2,3-*dihydro*-1H-*indazole*-1-*spiro*-1′-*piperidinium chloride* **20**. M.p. 184–186 °C (decomp.) [Found: C, 50.7; H, 5.0; Cl, 12.6; N, 15.1. $C_{12}H_{14}ClN_3O_3$ (283.7) requires C, 50.8; H, 5.0; Cl, 12.5; N, 14.8%]; $\delta_H(D_2O)$ 8.52 (1 H, dd, J_o 9, J_m 2, 6-H), 8.44 (1 H, d, J_m 2, 4-H), 8.08 (1 H, d, J_o 9, 7-H), 4.01 [2 H, m, J_{gem} (−)13, $J_{a,a}$ 13, $J_{a,e}$ 3, NCH_a], 3.28 [2 H, br d, J_{gem} (−)13, NCH_e] and 2.20–1.50 (6 H, m, $C[CH_2]_3C$); $\delta_C(D_2O)$ 170.65 (C-3), 158.18 (C-7a), 151.56 (C-5), 130.34 (C-4), 128.68 (C-3a), 121.42 and 120.39 (C-6 and -7), 68.20 (NCH_2) and 22.80 and 21.06 ($C[CH_2]_3C$).

1,1-*Dimethyl*-3-*oxo*-2,3-*dihydro*-1H-*indazolium chloride* **21**. M.p. 166–168 °C (decomp.) (from MeOH) [Found: C, 54.2; H, 5.8; Cl, 17.9; N, 14.0. $C_9H_{11}ClN_2O$ (198.65) requires C, 54.4; H, 5.6; Cl, 17.85; N, 14.1%]; $\delta_H(D_2O)$ 8.0–7.7 (4 H, m, ArH) and 3.66 (6 H, s, Me).

3-*Oxo*-2,3-*dihydro*-1H-*indazole*-1-*spiro*-1′-*piperidinium chloride* **22**. M.p. 166–169 °C (decomp.) (from EtOH) [Found: C, 60.15; H, 6.55; Cl, 14.9; N, 11.5. $C_{12}H_{15}ClN_2O$ (238.7) requires C, 60.4; H, 6.3; Cl, 14.85; N, 11.7%]; $\delta_H(D_2O)$ 7.90–7.60 (4 H, m, ArH), 4.07 [2 H, m, J_{gem} (−)13, $J_{a,a}$ 13, $J_{a,e}$ 3, NCH_a], 3.42 [2 H, br d, J_{gem} (−)13, NCH_e] and 2.20–1.50 (6 H, m, $C[(CH_2]_3C$); $\delta_C(D_2O)$ 169.23 (C-3), 153.47 (C-7a), 136.95 (C-4), 134.12 (C-5), 126.48 (C-6), 123.59 (C-3a), 118.68 (C-7), 69.19 (NCH_2) and 22.55 and 20.65 ($C[CH_2]_3C$).

3-*Oxo*-2,3-*dihydro*-1H-*indazole*-1-*spiro*-1′-*azepanium chloride* **23**. M.p. 158–161 °C (decomp.) (from EtOH) [Found: C, 62.0; H, 7.0; Cl, 14.3; N, 11.25. $C_{13}H_{17}ClN_2O$ (252.75) requires C, 61.8; H, 6.8; Cl, 14.0; N, 11.1%]; $\delta_H(D_2O)$ 7.90–7.50 (4 H, m, ArH), 4.09 (2 H, m, NCH_A), 3.61 (2 H, m, NCH_B) and 2.01 and 1.71 (both 4 H and br s, $C[CH_2]_4C$).

1,2-*Disubstituted and Condensed Indazolinones*.—The characteristic band[11] of indazolinones [ν_{max}(Nujol)/cm^{-1} ~1665 (CO)] was found in the IR spectra of these compounds.

2-*Nitro*-6,7,8,9-*tetrahydro*-11H-*pyridazino*[1,2-a]*indazol*-11-*one* **24**. [Found: C, 56.4; H, 4.9; N, 18.2. $C_{11}H_{11}N_3O_3$ (233.2) requires C, 56.65; H, 4.75; N, 18.0%]; $\delta_C(CDCl_3)$ 159.87 (C-11), 150.3 (C-4a). 142.46 (C-2), 126.75 (C-3), 121.01 (C-1), 117.95 (C-11a), 110.66 (C-4), 48.81 (C-6), 41.23 (C-9) and 22.63 and 22.08 (C-7 and -8); *m*/*z* 233 (M^+, 100%), 187 (35), 131 (13), 130 (12), 103 (11), 76 (17) and 75 (23).

2-*Nitro*-7,8,9,10-*tetrahydro*-6H,12H-[1,2]*diazepino*[1,2-a]*indazol*-12-*one* **25**. Data for this compound have been previously reported by us.[1,12]

7,8,9,10-*Tetrahydro*-6H,12H-[1,2]*diazepino*[1,2-a]*indazol*-12-*one* **26**. [Found: C, 71.1; H, 6.8; N, 14.0. $C_{12}H_{14}N_2O$ (202.25) requires C, 71.3; H, 7.0; N, 13.85%]; $\delta_C(CDCl_3)$ 159.61 (C-12), 145.27 (C-4a), 131.01 (C-3), 123.24 (C-1), 120.18 (C-2), 116.27 (C-12a), 109.46 (C-4), 50.38 (C-6), 42.72 (C-10) and 28.68, 27.65 and 27.39 (C-7, -8 and -9); *m*/*z* 202 (M^+, 100%), 187 (12), 173 (25), 147 (47), 146 (48), 134 (36), 132 (18), 119 (24), 104 (22), 91 (14) and 77 (47).

2-*Nitro*-6,11-*dihydro*-13H-*indazolo*[1,2-b]*phthalazin*-13-*one* **27**. [Found: C, 64.1; H, 3.7; N, 15.0. $C_{15}H_{11}N_3O_3$ (281.3) requires C, 64.05; H, 3.9; N, 14.9%]; $\delta_C(CDCl_3)$ 161.13 (C-13), 150.69 (C-4a), 143.25 (C-2), 128.31, 128.28, 127.94, 127.76, 127.35, 126.96 and 126.54 (C-3, -6a, -7, -8, 9, -10 and -10a), 121.43 (C-1), 118.77 (C-13a), 111.36 (C-4), 50.48 (C-6) and 43.85 (C-11); *m*/*z* 281 (M^+, 100%), 280 (52), 235 (11), 234 (21), 206 (10), 104 (99), 103 (32), 78 (27), 77 (14) and 75 (23).

2-*Nitro*-6,17-*dihydro*-12H-*indazolo*[2,1-b][2,3]*benzodiazepin*-14-*one* **28**. [Found: C, 64.9; H, 4.4; N, 14.3. $C_{16}H_{13}N_3O_3$ (295.3) requires C, 65.1; H, 4.4; N, 14.2%]; $\delta_C(CDCl_3)$ 161.24 (C-14), 151.24 (C-4a), 142.98 (C-2), 139.17 and 134.83 (C-7a and 11a), 129.62, 129.07, 128.70, 127.64 and 127.42 (C-3, -8, -9, -10 and -11), 121.45 (C-1), 118.21 (C-14a), 111.44 (C-4), 52.03 (C-6), 48.41 (C-12) and 33.78 (C-7); *m*/*z* 295 (M^+, 100%), 294 (75), 248 (25), 118 (13), 117 (36), 115 (24), 104 (45), 103 (17), 91 (18), 78 (12) and 75 (12).

1,2-*Dimethyl*-5-*nitro*-1,2-*dihydro*-3H-*indazol*-3-*one* **34**. $\delta_C(CDCl_3)$ 161.00 (C-3), 149.82 (C-7a), 142.18 (C-5), 127.08 (C-6), 121.20 (C-4), 116.99 (C-3a), 110.45 (C-7), 35.48 [N(1)Me] and 28.97 [N(2)Me].

2-*Nitro*-11,12-*dihydro*-6H,14H-*indazolo*[1,2-b][2,3]*benzodiazepin*-14-*one* **46**. [Found: C, 65.2; H, 4.2; N, 14.3. $C_{16}H_{13}N_3O_3$ (295.3) requires C, 65.1; H, 4.4; N, 14.2%]; $\delta_C(CDCl_3)$ 161.59 (C-14), 150.82 (C-4a), 142.96 (C-2), 139.94 and 133.55 (C-6a and -10a), 130.12, 129.28, 129.22, 127.52 and 127.46 (C-3, -7, -8, -9 and -10), 121.54 (C-1), 118.14 (C-14a), 111.53 (C-4), 57.30 (C-6), 44.18 (C-12) and 33.95 (C-11); *m*/*z* 295 (M^+, 100%), 294 (15), 280 (15), 239 (28), 178 (6), 117 (84), 104 (55), 77 (17) and 75 (13).

N′,N′-*Disubstituted* 2-*Methoxy*-5-*nitrobenzohydrazides*.—2-*Methoxy*-N′,N′-*dimethyl*-5-*nitrobenzohydrazide* **29**. M.p. 133–136 °C (from Pr^{i}OH) [Found: C, 50.3; H, 5.2; N, 17.7. $C_{10}H_{13}N_3O_4$ (239.2) requires C, 50.2; H, 5.5; N, 17.6%]; $\delta_H(CDCl_3)$ 9.03 (*Z* rot.) (1 H, d, J_m 3, 6-H), 8.31 (*Z*) (1 H, dd, J_o 9, J_m 3, 4-H), 7.09 (*Z*) (1 H, d, J_o 9, 3-H), 4.11 (*Z*) and 3.98 (*E*) (3 H, s, OMe) and 2.75 (*Z*) and 2.49 (*E*) (6 H, s, NMe_2) (*Z*/*E* ratio 96:4); $\delta_H[(CD_3)_2SO]$ 3.96 (*Z*) and 3.92 (*E*) (3 H, s, OMe), and 2.56 (*Z*) and 2.36 (*E*) (6 H, s, NMe_2) (*Z*/*E* ratio 65:35); $\delta_C[(CD_3)_2SO]$ 56.94 (*Z*) and 56.40 (*E*) (OMe) and 47.47 (*E*) and 46.23 (*Z*) (NMe_2).

2-*Methoxy*-5-*nitro*-N-*piperidinobenzamide* **31**. This compound has been previously mentioned, without m.p. and spectral data, in a preliminary communication;[1] m.p. 153–155 °C (from Pr^{i}OH); $\delta_H(CDCl_3)$ 8.99 (*Z* rot.) (1 H, d, J_m 3, 6-H), 8.32 (*Z*) (1 H, dd, J_o 9, J_m 3, 4-H), 7.09 (*Z*) (1 H, d, J_o 9, 3-H), 4.10 (*Z*) and 3.96 (*E*) (3 H, s, OMe), 2.92 (*Z*) (4 H, t, NCH_2) and 1.76 and 1.47 (*Z*) (6 H, both m, $C[CH_2]_3C$) (*Z*/*E* ratio 96:4).

2-*Methoxy*-5-*nitro*-N-*trimethylammoniobenzamidate* **30**. M.p. 178–180 °C (from benzene) [Found: C, 52.4; H, 5.95; N, 16.7. $C_{11}H_{15}N_3O_4$ (253.3) requires C, 52.2; H, 6.0; N, 16.6%]; $\delta_H(CDCl_3)$ 8.26 (1 H, d, J_m 3, 6-H), 8.15 (1 H, dd, J_o 9, J_m 3, 4-H), 6.90 (1 H, d, J_o 9, 3-H), 3.92 (3 H, s, OMe) and 3.50 (9 H, s, $\overset{+}{N}Me_3$).

1,2,3,4,4a,5-*Hexahydro*-6H-*pyrido*[1,2-a]*quinazolin*-6-*one* **33**. M.p. 184–186 °C (from Pr^{i}OH) (lit.,[17] 182–185 °C); *m*/*z* 202 (M^+, 37%), 201 (63), 173 (32), 147 (13), 146 (100), 145 (16), 118 (13) and 77 (18).

3-*Alkoxy*-1-*alkyl*-1H-*indazoles*.—Characteristic bands[11] of 3-alkoxy-1-alkylindazoles [ν_{max}(Nujol)/cm^{-1} ~1620 and 1580 (C=C) and 1550 (C=N)] were found in the IR spectra of these compounds.

3-*Methoxy*-1-*methyl*-5-*nitro*-1H-*indazole* **35**. This compound has been previously mentioned, without m.p. and spectral data, in a preliminary communication;[1] m.p. 164–166 °C (from EtOH); $\delta_H(CDCl_3)$ 8.58 (1 H, d, J_m 3, 4-H), 8.20 (1 H, dd, J_o 9, J_m 3, 6-H), 7.20 (1 H, d, J_o 9, 7-H), 4.10 (3 H, s, OMe) and 3.92 (3 H, s, NMe); $\delta_C(CDCl_3)$ 158.14 (C-3), 142.94 (C-7a), 140.69 (C-5), 122.47 (C-6), 118.54 (C-4), 111.71 (C-3a), 108.43 (C-7), 56.50 (OMe) and 35.46 (NMe); *m*/*z* 207 (M^+, 100%), 192 (33), 177 (10), 161 (20), 150 (13), 146 (14), 104 (19) and 75 (18).

1,3′:1′,3-*Bis*(*tetramethyleneoxy*)*bis*(5-*nitro*-1H-*indazole*) **36**. M.p. 273–275 °C (from pentan-1-ol) [Found: C, 56.4; H, 4.9; N, 18.0. $C_{22}H_{22}N_6O_6$ (466.45) requires C, 56.65; H, 4.75; N, 18.0%]; $\delta_H(CDCl_3)$ 8.29 (2 H, d, J_m 3, 4-H), 8.14 (2 H, dd, J_o 9, J_m 3, 6-H), 7.18 (2 H, d, J_o 9, 7-H), 4.42 (4 H, t, OCH_2), 4.26 (4 H,

t, NCH_2) and 2.03 and 1.93 (both 4 H, both m, $C[CH_2]_2C$); *m/z* 466 (M^+, 14%), 234 (52), 233 ($M^+/2$, 100), 232 (16), 192 (16), 187 (14), 146 (7), 103 (12), 89 (12), 76 (16) and 75 (19).

1,3′:1′,3-*Bis*(*pentamethyleneoxy*)*bis*(5-*nitro*-1H-*indazole*) **37**. M.p. 249–251 °C (from diglyme) [Found: C, 58.1; H, 5.15; N, 17.2. $C_{24}H_{26}N_6O_6$ (494.5) requires C, 58.3; H, 5.3; N, 17.0%]; $\delta_H(CDCl_3)$ 8.20 (2 H, d, J_m 3, 4-H), 8.15 (2 H, dd, J_o 9, J_m 3, 6-H), 7.15 (2 H, d, J_o 9, 7-H), 4.25 (4 H, t, OCH_2), 4.15 (4 H, t, NCH_2) and 1.95, 1.74 and 1.32 (all 4 H, all m, $C[CH_2]_3C$); *m/z* 494 (M^+, 16%), 248 (44), 247 ($M^+/2$, 100), 246 (14), 232 (10), 192 (36), 146 (30), 76 (12) and 75 (16).

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