SYNTHESIS BY PHASE TRANSFER CATALYSIS OF N-BENZYL, N-DIPHENYLMETHYL AND N-TRIPHENYLMETHYL AZOLES AND BENZAZOLES: PROTON NMR AND CHROMATOGRAPHIC DATA AS A TOOL FOR IDENTIFICATION

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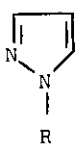
Abstract- Pyrazole, imidazole, 1,2,4-triazole, indazole and benzotriazole were alkylated under phase transfer catalysis (PTC) with benzyl-, diphenylmethyl- and trityl chloride. Alkylation occurred only at the ring nitrogen atoms of the heterocycle, except for indazole in which substitution took also place at position 3. A systematic study of the N- and C-substituted derivatives by proton NMR and chromatographic techniques has been done.

This work is concerned with the preparation of N-substituted derivatives of azoles, analogous to the widely used antifungal agent chlotrimazole[1].

All products studied are assembled in Scheme 1, unless 4c, 7a and 9c that had not been obtained in our reaction conditions: alkylation of the azole or its benzo derivative under liquid-liquid or solid-liquid phase transfer catalysis[2,3,4] using equimolecular amounts of the reactants (azole or benzazole 1 : alkylating agent 1), tetrabutylammonium bromide or bisulfate as catalyst and xylene as the solvent. For the reaction of azoles with simpler halides in the presence of PTC see reference 5.

When the starting materials were pyrazole, imidazole, 1,2,4-triazole and benzotriazole only N-substituted derivatives were formed with the three alkylating agents: benzyl-, diphenylmethyl and trityl chloride. Relative percentages showing the regioselectivity of the reaction are gathered in Table 1 and are in agreement with the general reactivity of five membered aromatic nitrogenated heterocycles that possess several nucleophilic sites[5].

1-Benzyl- and 2-benzylindazoles had been prepared previously by von Auwers[6] in 1921 from indazole and benzyl chloride in ethanol-sodium ethoxide. This author separates the two isomers and describes the physical characteristics of the bases and their picrates, but does not provide any chemical support to the assignment made. We have reprepared the picrate of 2-benzylindazole obtained by PTC, whose structure was confirmed by proton NMR spectroscopy, checking that the previous attribution made by von Auwers was correct.



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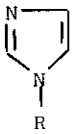

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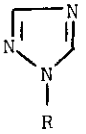

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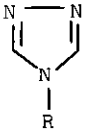

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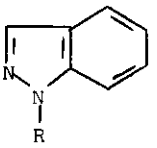

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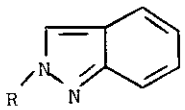

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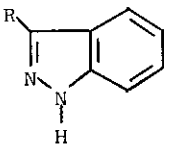

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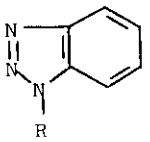

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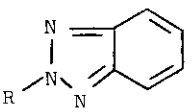


9

R

a $-CH_2C_6H_5$

b $-CH(C_6H_5)_2$

c $-C(C_6H_5)_3$

Surprisingly, when the reaction was done with indazole and diphenylmethyl or trityl chloride in the same PTC conditions, together with the N-alkylated products it was possible to isolate the derivatives 7b and 7c in which substitution reaction of indazole had occurred at the carbon atom in position 3. No examples of C-3 alkylation of indazole had been reported previously and the mechanism of this reaction is being investigated to check if it is ionic (SN_1) or radical. In addition certain reactions involving the triphenylmethyl cation, when an SN_1 mechanism would seem to be obviously indicated, it has been shown by esr detection of the intermediate that free radicals are actually involved[8].

It has also been reported by Habraken et al. that 1-nitro- and 2-nitroindazoles[9,10] can be converted in 3-nitro derivatives, but our attempts to transform the 1- or 2-substituted derivatives 5 and 6 into the 3-substituted ones 7 by heating in xylene or benzonitrile were unsuccessful.

Spectroscopic data

Proton NMR data of the various products are gathered in Tables 2 and 3 and the assignment of the signals to the different protons were made using the corresponding methyl derivatives as model compounds[3,11-15].

For pyrazole, imidazole and s-triazole derivatives attribution did not offer any difficulty, unless for protons H_3 and H_5 in 1-trityl-1,2,4-triazole 3c and protons H_5 and H_6 in 1-tritylbenzotriazole 8c, so close that they can be interverted.

Table 1. Regioselectivity in the alkylation reactions

Starting material	Alkylating agent	Total yield	Reaction products N-alkylation	C-alkylation
Pyrazole	$ClCH_2C_6H_5$	80%	1a (100%)	
	$ClCH(C_6H_5)_2$	70%	1b (100%)	
	$ClC(C_6H_5)_3$	55%	1c (100%)	
Imidazole	$ClCH_2C_6H_5$	76%	2a (100%)	
	$ClCH(C_6H_5)_2$	66%	2b (100%)	
	$ClC(C_6H_5)_3$	80%	2c (100%)	
1,2,4-Triazole	$ClCH_2C_6H_5$	88%	3a (85%); 4a (15%)	
	$ClCH(C_6H_5)_2$	34%	3b (70%); 4b (30%)	
	$ClC(C_6H_5)_3$	57%	3c (100%)	
Indazole	$ClCH_2C_6H_5$	80%	5a (60%); 6a (40%)	
	$ClCH(C_6H_5)_2$	65%	5b (38%); 6b (24%)	7b (38%)
	$ClC(C_6H_5)_3$	80%	5c (38%); 6c (15%)	7c (47%)
Benzotriazole	$ClCH_2C_6H_5$	95%	8a (85%); 9a (15%)	
	$ClCH(C_6H_5)_2$	95%	8b (90%); 9b (10%)	
	$ClC(C_6H_5)_3$	70%	8c (100%)	

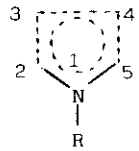
Pairs of isomers 3-4 and 8-9 are easily differentiated by proton NMR spectroscopy because of the symmetry of 1-substituted 1,3,4-derivatives 4 with two equivalent protons H_2 and H_5, and 2-substituted benzotriazoles 9 with an AA'BB' system.

It is necessary to remark that proton NMR spectra of 8b, 1-diphenylmethylbenzotriazole, had been described erroneously by Schmid et al.[14a] with a methine group (-CH-) appearing at 5.80 ppm. We have found that this proton appears at 7.38 ppm as it was previsible from the methylene group signal at 5.88 ppm in the 1-benzylbenzotriazole 8a.

Proton NMR spectra of 1-, 2- and 3-substituted indazoles 5c, 6c (ABCDE systems) and 7c (ABCD system) at 360 MHz were carefully analyzed with the PANIC 82 program and with aid of double irradiation experiments, obtaining chemical shifts (δ) and coupling constants (J) similar to the observed for 1-methyl-, 2-methyl- and 3-methylindazoles[7]. The excellent resolution allows to observe $J_{3,7}$ for 5c. Proton signals of compounds 5a-b, 6a-b and 7b were then assigned by analogy to the ones of 5c, 6c and 7c. The 2-tritylindazole 6c had been erroneously described as the 1-substituted indazole 5c but spectroscopic data confirm its structure[16].

The Shoolery additive model[17] was applied to the methyl, methylene and methine signals. In addition to the values of Tables 2 and 3, the benzimidazole derivatives[18] [1-methyl, 1-benzyl and 1-diphenylmethyl] and toluene[17] [δ CH_3: 2.35 ppm], diphenylmethane[17] [δ CH_2: 3.92 ppm] and triphenylmethane[17] [δ CH: 5.50 ppm] were also included. A multiple regression analysis (n = 30, R^2 = 0.998) yields the following values of the substituent shielding constants:

Table 2. Proton NMR chemical shifts (δ) and coupling constants (J) in $CDCl_3$ of substituted azoles



PRODUCT		H_2	H_3	H_4	H_5	-C-H	$-C_6H_5$
1-Methylpyrazole[3]		--	7.45	6.22	7.32	3.91	--
1a	-a-	--	7.54 (d) -b-	6.24 (t) -b-	7.05-7.29 -c-	5.57 (s)	7.05-7.29 (m, 5H)
1b	-d-	--	7.58 (d) $J_{3,4}$ = 2.02	6.25 (m)	7.24 (d) $J_{4,5}$ = 2.38	6.78 (s)	7.05-7.09 (m,4H); 7.25-7.34(m, 6H)
1c	-d-	--	7.66 (d) $J_{3,4}$ = 1.83	6.23 (m)	7.37 (d) $J_{4,5}$ = 2.56	--	7.10-7.18(m, 6H); 7.26-7.33(m,9H)
1-Methylimidazole[11]		7.33	--	6.95	6.83	3.55	--
2a	-a-	7.63 (bs) -c-	--	7.18 (bs) -c-	6.98 (bs) -c-	5.15 (s)	7.24-7.51 (m, 5H)
2b	-d-	7.38 (s)	--	7.05-7.15 -d-	6.83 (s)	6.51 (s)	7.05-7.15(m,4H); 7.32-7.37(m,6H)
2c	-d-	7.46 (t) $J_{2,4}$ = 1.2	--	7.06 (t) $J_{4,5}$ = 1.2	6.82 (t) $J_{2,5}$ = 1.2	--	7.09-7.20(m,6H); 7.26-7.37(m,9H)

Table 2 (Cont.)

PRODUCT	H_2	H_3	H_4	H_5	-C-H	$-C_6H_5$
1-Methyl-1,2,4-triazole[12]	--	8.10	--	7.83	3.87	--
3a -d-	--	8.06 (s)	--	7.94 (s)	5.30 (s)	7.20-7.24(m,2H); 7.30-7.36(m,3H)
3b -a-	--	7.92 (s)	--	8.05 (s)	6.76 (s)	7.03-7.47 (m, 10H)
3c -d-	--	8.02 (s)	--	8.07 (s)	--	7.11-7.16(m,6H); 7.32-7.36(m,9H)
1-Methyl-1,3,4-triazole[12]	8.24 (s)	--	--	8.24	3.83	--
4a -d-	8.18 (s)	--	--	8.18 (s)	5.20 (s)	7.17-7.20(m,2H); 7.35-7.39(m,3H)
4b -d-	8.04 (s)	--	--	8.04 (s)	6.60 (s)	7.10-7.13(m,4H); 7.36-7.41(m,6H)

-a- Field frecuency 90 MHz

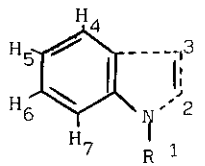
-b- Coupling constant J could not be measured due to bad resolution

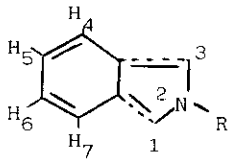
-c- Proton signal masked by the phenyl group

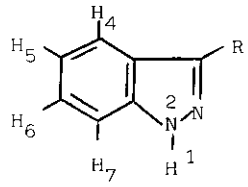
-d- Field frecuency 300 MHz

s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet

Table 3. Proton NMR chemical shifts (δ) and coupling constants (J) in $CDCl_3$ of substituted benzazoles







PRODUCT	H_3	H_4	H_5	H_6	H_7	-C-H	$-C_6H_5$
1-Methyl--indazole[13]	7.95	7.72	7.10	7.35	7.51	4.02	--
5a -a-	8.03(bs)	7.70(d) $J_{4,5}$=8.1	7.08-7.32 -b-	7.08-7.32 -b-	7.08-7.32 -b-	5.55(s)	7.08-7.32 (m,5H)
5b -a-	8.07(bs)	7.70 (d) $J_{4,5}$=8.05	7.06-7.13 (m)	7.06-7.13 (m)	7.15-7.32 -b-	7.03(s)	7.15-7.32 (m,10H)
5c -a-	8.07(d) $J_{3,7}$=0.95	7.67(d) $J_{4,5}$=7.8	7.02 (q) $J_{5,6}$ = 6.9	6.95(q) $J_{6,5}$ = 6.9	6.48 (m) $J_{6,7}$=8.4	--	7.17-7.27 (m,15H)

Cont.

Table 3 (Cont.)

PRODUCT	H_3	H_4	H_5	H_6	H_7	-C-H	$-C_6H_5$
1-Methylbenzo--triazole[14]	--	7.93	7.25	7.32	7.37	4.28	--
8a -a-	--	8.05(m) $J_{4,5}$=7.71 $J_{4,6}$=1.31	7.25-7.45 -b-	7.25-7.45 -b-	7.25-7.45 -b-	5.88(s)	7.25-7.45 (m, 5H)
8b -a-	--	8.06(m)	7.28-7.35	7.28-7.35 -b-	7.08(m)	7.38(s)	7.19-7.24(m,4H);7.28-7.35(m,6H)
8c -a-	--	8.05(d) $J_{4,5}$=8.40	7.14-7.31	7.08(m)	6.42(d) $J_{7,6}$=8.50	--	7.14-7.31 (m, 15H)
2-Methyl-indazole[13]	8.05	7.63	6.99	7.19	7.63	4.13	--
6a -a-	7.80(s)	7.58(d) $J_{4,5}$=8.3	7.04(m)	7.19-7.32 -b-	7.72(d) $J_{7,6}$=8.7	5.51(s)	7.19-7.32 (m, 5H)
6b -a-	7.72(s)	7.59(d) $J_{4,5}$=8.3	7.02-7.13 -b-	7.23-7.36 -b-	7.72(d) $J_{6,7}$=8.8	7.09(s)	7.02-7.13(m,4H);7.23-7.36(m,6H)
6c -a-	7.88(s)	7.59(d) $J_{4,5}$=8.2	7.06(m)	7.16-7.38 -b-	7.73(d) $J_{6,7}$=8.8	--	7.16-7.38 (m, 15H)

Cont.

Table 3 (Cont.)

PRODUCT	H_3	H_4	H_5	H_6	H_7	-C-H	$-C_6H_5$
2-Methyl-benzo--triazole[14]	--	7.94	7.37	7.37	7.94	4.50	--
9a -a-	--	7.84 (m) $J_{4,5}$=6.5 $J_{4,6}$=3.15	7.41-7.37	7.41-7.37	7.84 (m) $J_{6,7}$=6.5 $J_{5,7}$=3.15	5.87(s)	7.27-7.32(m,3H); 7.35-7.41(m,2H)
9b -a-	--	7.88 (m) $J_{4,5}$=6.6 $J_{4,6}$=2.98	7.29-7.39 -b-	7.29-7.39 -b-	7.88 (m) $J_{6,7}$=6.6 $J_{5,7}$=2.98	7.35 (s)	7.24-7.39 (m, 10H)
3-Methyl--indazole[15]	--	7.64	7.10	7.32	7.40	2.63	--
7b	--	6.98 (m)	7.18-7.30 -b-	7.18-7.30 -b-	7.18-7.30 -b-	5.92 (s)	7.18-7.30 (m, 10H)
7c	--	6.48 (d) $J_{4,5}$= 8.1	6.76 (m)	7.11-7.27 -b-	7.50 (d) $J_{6,7}$= 8.2	--	7.11-7.27 (m, 15H)

-a- Field frecuency 300 MHz

-b- Proton signal masked by the phenyl group

Constant : 0.97 ± 0.05
Pyrazol-1-yl : 2.87 ± 0.06
Imidazol-1-yl : 2.62 ± 0.06
1,2,4-Triazol-1-yl : 2.86 ± 0.06
1,3,4-Triazol-1-yl : 2.76 ± 0.06
Indazol-1-yl : 3.09 ± 0.06
Indazol-2-yl : 3.13 ± 0.06
Benzotriazol-1-yl : 3.40 ± 0.06
Benzotriazol-2-yl : 3.46 ± 0.06
Benzimidazol-1-yl : 2.82 ± 0.06
Phenyl : 1.48 ± 0.02

Thus, for example, the chemical shift of the methine group in 1-diphenylmethylindazole 5b would be calculated as 0.97 + 3.09 + (2 x 1.48) = 7.02 ppm and compared to the actual value of 7.03 ppm (Table 3). The largest discrepancies are found for literature values: toluene (calculated: 2.45 ppm) and triphenylmethane (calculated: 5.40 ppm). As it can be seen the azoles produce larger effects than the phenyl and these effects become more important when α-nitrogen atoms and fused benzene rings are present in its structure.

Chromatographic data

Rf values of the several derivatives in chloroform/acetonitrile (95:5) are shown in Table 4. The compounds 5c and 6c had the same Rf value in this eluent and chloroform was used to distinguish them by thin layer chromatography. New Rf values in this solvent were: 5c (0.29), 6c (0.18) and 7c (0.07).

Table 4. Rf values of substituted azoles and benzazoles

Product	Rf	Product	Rf	Product	Rf
1a	0.31	1b	0.46	1c	0.57
2a	0.08	2b	0.08	2c	0.18
3a	0.10	3b	0.13	3c	0.31
4a	0.02	4b	0.03	4c	-
5a	0.48	5b	0.54	5c	0.60
6a	0.36	6b	0.48	6c	0.60
7a	-	7b	0.27	7c	0.38
8a	0.36	8b	0.44	8c	0.51
9a	0.53	9b	0.55	9c	-

Statistical analysis of the benzyl- and trityl-derivatives Rf's against diphenylmethyl derivatives Rf's showed that these data were related by the following lineal equations:

$$Rf\ (benzyl) = 0.85\ Rf\ (diphenylmethyl),\ R = 0.974$$

and

$$Rf\ (trityl) = 0.15 + 0.88\ Rf\ (diphenylmethyl),\ R = 0.981$$

This second equation includes also the 3-substituted indazoles 7b and 7c. Rf of the diphenylmethyl compounds have been chosen as independent variables because they correspond to the series with the largest number of data, the more complete in subs-

tituted azoles and benzazoles.

EXPERIMENTAL

Melting points were determined in a capillary tube and are uncorrected. All the new compounds described in this paper give correct analytical results (C, H, N) for the calculated empirical formulae within ±0.3%.
Proton NMR spectra were obtained with Varian XL-300 (300 MHz) and EM-390 (90 MHz) spectrometers. Chemical shifts (δ) in ppm and coupling constants (J) in Hz were measured in $CDCl_3$ referred to TMS as an internal standard.
Analytical thin layer chromatography has been performed on silica gel Alugram Sil G/UV_{254} with a thickness layer of 0.25 mm. Column chromatography with silica gel Merck 60 (70-230 mesh, ASTM) and with the eluent indicated in each case (Table 5). Unless for the benzyl derivatives anhydrous solvents without acidic hydrogens as xylene, benzene, chloroform (stabilized with amilene) and acetonitrile have been used to avoid decomposition of the products.

General Alkylation Procedure

Most of the compounds were prepared by method A, except derivatives 2c and 3c that were obtained by method B and 3b and 4b by the two methods with similar results. In both procedures (A and B) the crude product of the reaction was analyzed by proton NMR spectroscopy.

Method A : In a round bottomed flask provided with a refrigerant with a calcium chloride tube and magnetic stirring were introduced in the following order: 200 ml of xylene, 30 mmoles of azole or benzazole, 30 mmoles of anhydrous potassium carbonate, 30 mmoles of powdered potassium hydroxide, 1.5 mmoles of tetrabutylammonium salt (bromide or sulfate) and 30 mmoles of an alkylating agent. After 14-20 hours of heating under reflux, the hot reaction mixture was filtered and the residue washed twice with 25 ml of warm xylene. The solution was dried over anhydrous sodium sulfate and then isolation method indicated on Table 5 was applied in each case.

Method B : A suspension of finely divided 30 mmoles of sodium metal in 200 ml of xylene was heated under reflux. Addition of 30 mmoles of the powdered azole over the melted sodium allowed to get the corresponding azole sodium salt after heating during 15 h. Then 1.5 mmoles of tetrabutylammonium salt and 30 mmoles of alkylating agent were added and the reaction heated for 8 h more. After this time, the solution was filtered and the residue washed with three times 10 ml of xylene. The overall organic layers were treated as indicated on Table 5 to isolate pure compounds.

Table 5. Experimental conditions and physical characteristics of alkylated azoles and benzazoles.

Product	mp (°C)	Isolation	Yield (%)
1a	oil Lit (19): Eb_{15mm}=120	(a)	80
2a	68 Lit (20) : 70-72	(a)	76
3a	54 Lit (21) : 54	(b)	76

Table 5. (cont.)

4a	112 Lit (22) : 114-115	(b)	12
5a	oil Lit (6) : 64.5	(a)	48
6a	oil, picrate 158 (ethanol) Lit (6) : 71, picrate 163	(a)	32
8a	114-117 Lit (14) : 115-116	(a)	81
9a	oil Lit (23) : 36.5-37.5	(a)	14
1b	48-51	(c)	70
2b	79-81 Lit (24) : 206	(d)	66
3b	92-94	(e)	24
4b	157-159	(e)	10
5b	oil	(f)	25
6b	112-115 (hexane)	(a)	15
7b	123-125 (hexane)	(c)	25
8b	149-151 Lit (14) : 156-157	(g)	85
9b	oil	(a)	10
1c	202-204 Lit (25) : 202-202.5	(g)	55
2c	210-212 Lit (24) : 220	(g)	80
3c	213-216 Lit (26) : 210-211	(g)	57
5c	145-147	(a)	30
6c	179-180 Lit (16) : 180-182	(a)	12
7c	230	(g)	38
8c	214-216 Lit (27) : 224	(g)	70

Column chromatography on silica gel with: (a) chloroform, (b) chloroform-ethanol (95:5), (c) chloroform-acetonitrile (9:1), (d) chloroform-acetonitrile (7:3), (e) chloroform-acetonitrile (1:1) and (f) benzene; (g) Direct crystallization from the reaction mixture.

ACKNOWLEDGEMENTS

We thank Mrs. M.D. Casado and M. Plaza for recording the NMR spectra.

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Received, 2nd August, 1985