THE REACTION BETWEEN BENZOTRIAZOLE AND DIARYLNITRILEIMINES

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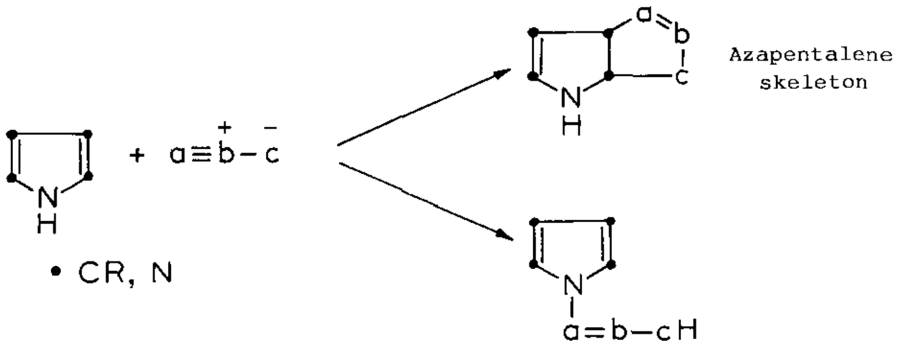
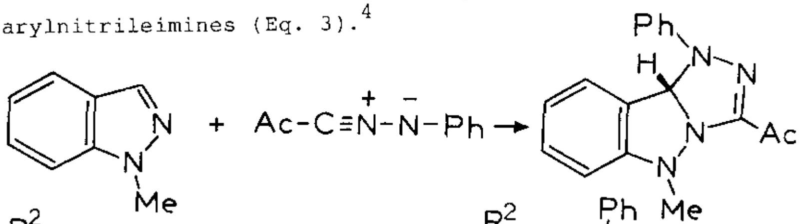
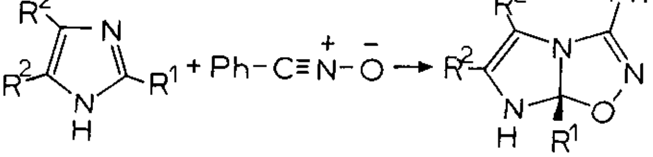
Abstract- The reaction between benzotriazole and diarylnitrileimines yielded the arylhydrazones of 1- and 2-benzotriazole. The structures were established through detailed studies by ^1H and ^{13}C nmr spectroscopies.

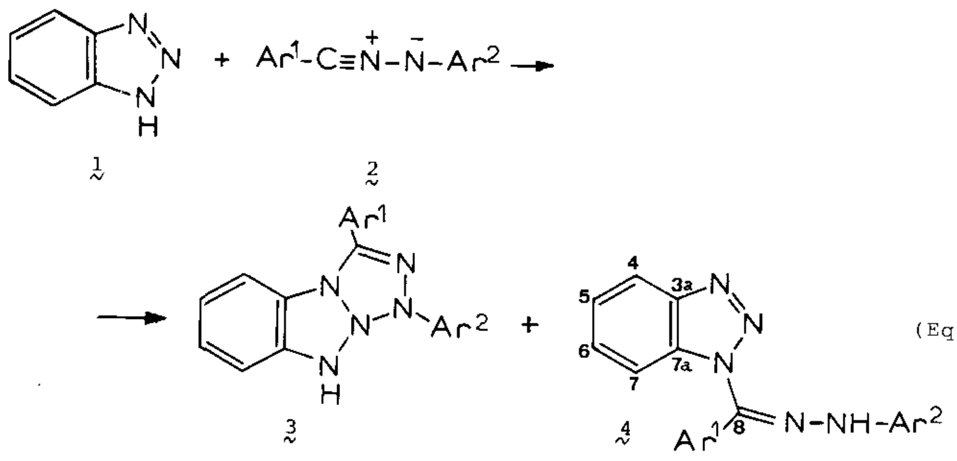
1,3-Dipoles can react with N-unsubstituted azoles in two ways: either to give a cycloaddition product by reaction with a formal double bond or an N-substituted derivative by electrophilic attack on the nitrogen. Both possibilities have been observed.



The first reaction was observed mainly with pyrroles and indoles (generally N-substituted).[1] A few reactions of other ring systems described in literature are; i) the reaction of 1-methylindazole with a nitrileimine (Eq. 1),[2] ii) the reaction of NH-imidazoles with benzonitrile oxide (Eq. 2),[3] iii) the reaction of benzotriazole with diarylnitrileimines (Eq. 3).[4]

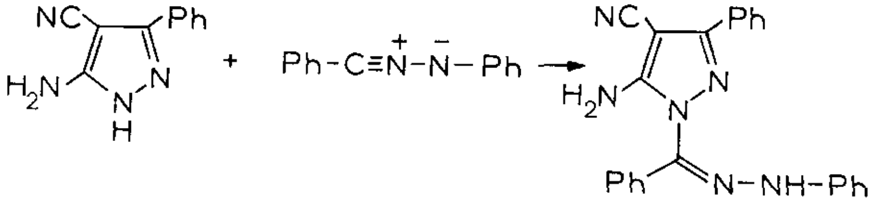

(Eq. 1)


(Eq. 2)



(Eq. 3)[4]

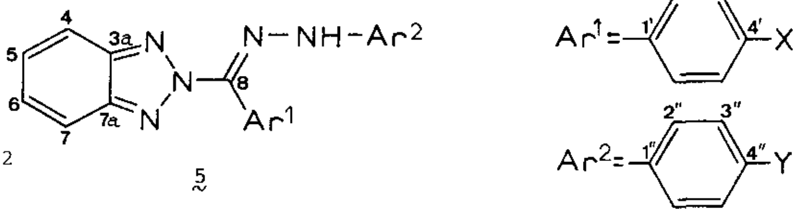
The second reaction has not been systematically studied (except for the N-methylation of azoles with diazomethane), but some examples can be found in the literature (Eq. 3 and 4).



(Eq. 4)[5]

As shown in Eq. 3, Sayanna et al.[4] reported that reactions of benzotriazole 1 with diarylnitrileimines 2 afforded cycloadducts 3 and 1-substituted products 4. However the structure of compound 3 is quite unexpected; it is the first example of a tetrazolo[1,2-a]benzotriazole,[1a] which is non-aromatic and possesses four linked sp^3 nitrogens. Taking into account that in the reaction of 1 with 2 there is possible an alternative structure for compound 3, namely the 2-substituted isomer 5, the nmr (^1H and ^{13}C) spectroscopic study of the products obtained in the reaction was carried out.

1 + 2 ⟶ 3 + 4 or 4 + 5



a, X = Y = H
b, X = H, Y = Me
c, X = H, Y = NO_2
d, X = Me, Y = H

5

The spectra were recorded in dimethyl sulphoxide at 300 MHz for the proton and 75 MHz for the carbon-13 (Varian XL-300); all values are in ppm from internal TMS (δ scale).

Table 1. Proton chemical shifts

No	4	5	6	7	2'	3'	4'	2"	3"	4"	Substit.
4a	8.30	~7.60	~7.60	7.41	~7.25	~7.35	~7.35	7.13	~7.25	6.89	----
4b	8.32	~7.60	~7.60	7.42	~7.15	~7.35	~7.35	7.10	7.20	----	2.26
4c	8.34	~7.60	~7.60	~7.40	~7.20	~7.40	~7.40	7.43	8.20	----	----
4d	8.31	~7.60	~7.60	7.41	7.05	7.20	----	~7.20	~7.30	6.89	2.31
5a	8.12	7.60	7.60	8.12	~7.30	~7.40	~7.40	~7.20	~7.30	6.89	----
5b	8.11	7.60	7.60	8.11	~7.30	~7.40	~7.40	7.10	7.20	----	2.24
5c	8.15	7.64	7.64	8.15	~7.25	~7.40	~7.40	7.46	8.20	----	----
5d	8.12	7.60	7.60	8.12	7.10	7.20	----	~7.25	~7.30	6.89	2.32

The complexity of the aromatic protons does not prevent the observation of the AA' BB' system characteristic of a 2-substituted benzotriazole[6] which is only consistent with structure 5.

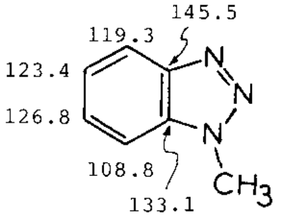
The carbon-13 nmr spectra definitely prove that the compounds resulting from the reaction of benzotriazole 1 with diarylnitrileimines 2 are positional isomers 4 and 5: the chemical shifts of the *N*-substituents are almost identical. The assignment of the heterocyclic carbons is based on literature results[7] for benzotriazoles carrying other substituents on the nitrogen. The chemical shifts found for compounds 4 and 5 are closely to those of *N*-methyl derivatives 6 and 7, respectively.

Table 2. Carbon-13 chemical shifts

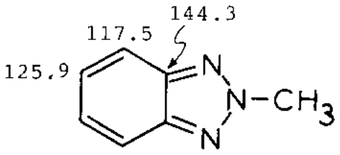
No	4	5	6	7	3a	7a	1'	2'
4a	119.9	124.6	128.8	110.1	145.0	133.0	133.7	124.5
4b	119.8	124.6	128.6	110.2	145.0	133.0	133.9	124.4
4c	120.0	124.9	129.2	110.2	145.0	133.0	133.0	125.5
4d	119.9	124.8	129.0	110.4	145.2	133.2	131.2	124.8
5a	118.7	125.1	125.1	118.7	144.3	144.3	133.5	127.7
5b	118.7	124.9	124.9	118.7	144.3	144.3	133.5	127.6
5c	118.8	125.9	125.9	118.8	144.4	144.4	133.4	128.0
5d	118.7	125.0	125.0	118.7	144.3	144.3	130.8	127.6

No	3'	4'	1"	2"	3"	4"	8	Substit.
4a	128.8	129.0	144.0	113.5	128.8	120.7	126.7	----
4b	128.8	129.4	141.8*	113.4	129.5	141.7*	126.0	20.2
4c	129.0	130.0	149.5	113.1	125.7	140.1	131.1	----
4d	129.7	138.8	144.3	113.6	129.2	120.7	127.1	20.9
5a	128.6	129.6	143.8	113.5	129.1	120.9	128.7	----
5b	128.6	129.6	141.5*	113.4	129.5	141.4*	129.0	20.2
5c	128.7	129.9	149.4	113.2	125.7	140.2	132.6	----
5d	129.0	138.4	143,9	113.4	129.1	120.6	129.8	20.8

*Assignments can be reversed



6[7]



7[7]

Carbon C_8 appears around 130 ppm, much higher than standard ketone phenylhydrazones (around 160 ppm),[8] due to the effect of the benzotriazole. A similar shielding is observed when acetone (δ C=O : 205.1 ppm)[9] is compared with 1-acetylbenzotriazole (δ C=O : 169.3 ppm).[7]

In conclusion, we can assert that, with the possible exception of imidazoles (Eq. 2), N-unsubstituted diazoles, triazoles and tetrazoles react with 1,3-dipoles as nucleophiles and not as dipolarophiles.

Compounds 4a and 5a are formally phenylhydrazones of 1- and 2-benzoylbenzotriazole. It is interesting to notice that, since acylation of azoles under thermodynamic control[6,7] is known to give only 1-acylbenzotriazoles, compounds 5 are derivatives of a new class of compounds, the 2-acylbenzotriazoles.

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