

THE REACTION BETWEEN BENZOTRIAZOLE AND DIARYLNITRILEIMINES

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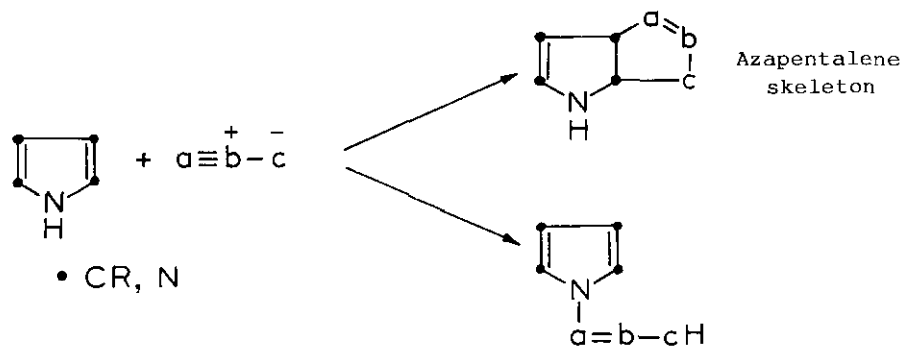
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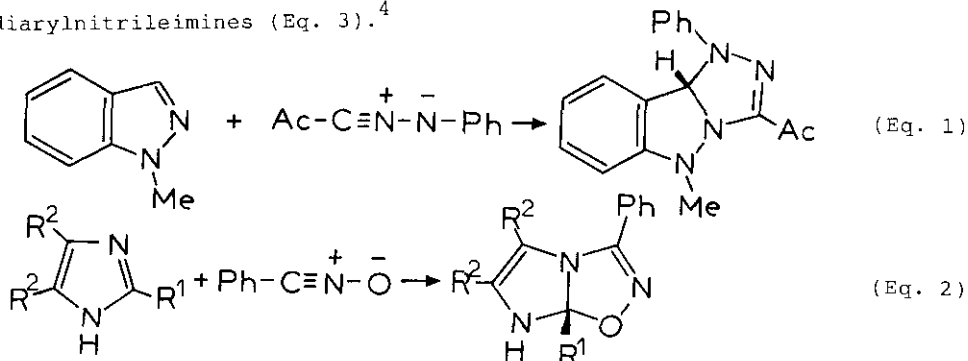
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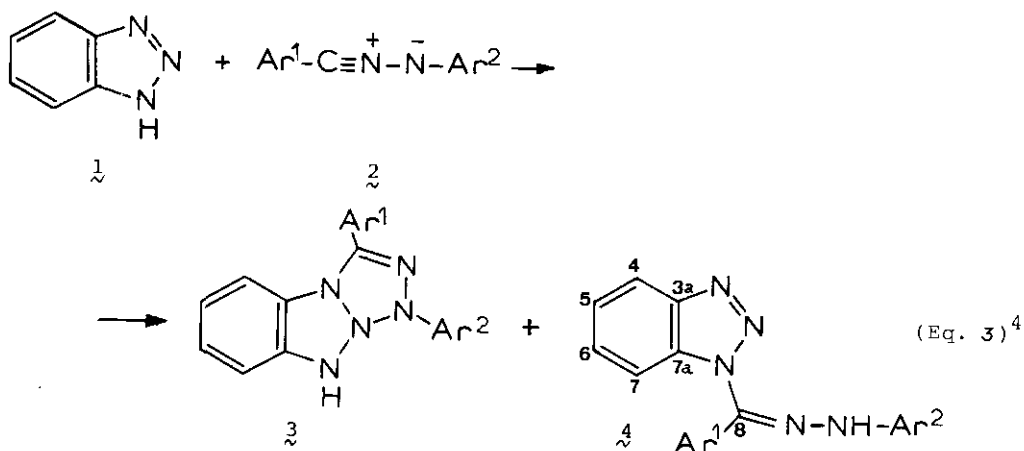
Abstract- The reaction between benzotriazole and diarylnitrile-imines yielded the arylhydrazones of 1- and 2-benzotriazole. The structures were established through detailed studies by ^1H and ^{13}C nmr spectroscopies.

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.

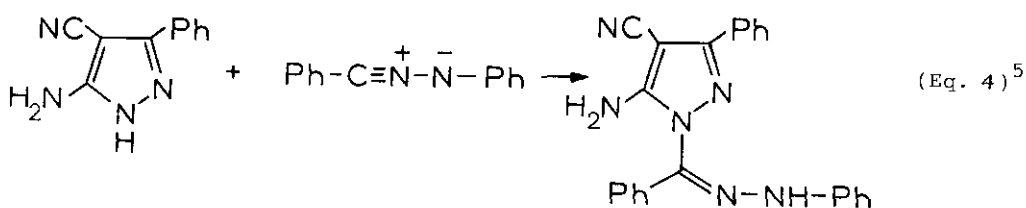


The first reaction was observed mainly with pyrroles and indoles (generally *N*-substituted).¹ A few reactions of other ring systems described in literature are; i) the reaction of 1-methylindazole with a nitrileimine (Eq. 1),² ii) the reaction of *NH*-imidazoles with benzonitrile oxide (Eq. 2),³ iii)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

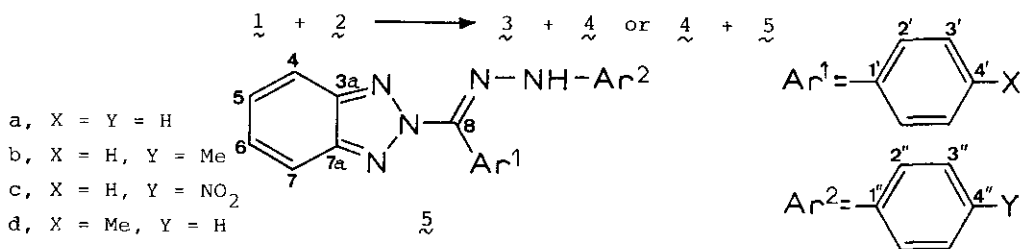




The second reaction has not been systematically studied (except for the *N*-methylation of azoles with diazomethane), but some examples can be found in the literature (Eq. 3 and 4).



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 ¹³C) spectroscopic study of the products obtained in the reaction was carried out.



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 benzotriazole⁶ which is only consistent with structure 5.

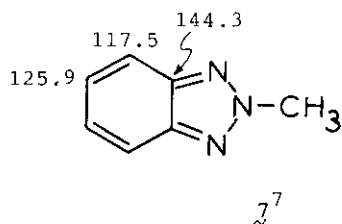
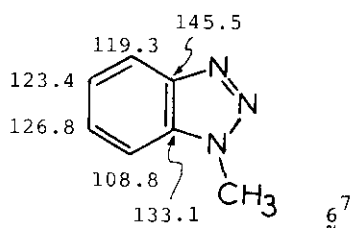
The carbon-13 nmr spectra definitely prove that the compounds resulting from the reaction of benzotriazole 1 with diarylnitrileimines 2 are positional isomers 4 and 5; the chemical shifts of the N-substituents are almost identical. The assignment of the heterocyclic carbons is based on literature results⁷ 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



Carbon C₈ 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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REFERENCES

- 1.a) J. Elguero, R.M. Claramunt and A.J.H. Summers, Adv. Heterocycl. Chem., 1978, 22, 183; b) A.S. Shawali and C. Parkanyi, J. Heterocycl. Chem., 1980, 17, 833; c) R.A. Jones, in 'Comprehensive Heterocyclic Chemistry' (A.R. Katritzky and C.W. Rees, Eds.), Pergamon Press, Oxford, 1984, 4, 262.
2. M. Ruccia, N. Vivona and G. Cusmano, Heterocycles, 1976, 4, 1655.
3. F. Foti, G. Grassi, F. Risitano and F. Caruso, J. Chem. Res. (S), 1983, p. 230.
4. E. Sayanna, R.V. Venkataratnam and G. Thyagarajan, Heterocycles, 1984, 22, 1561.
5. G.E.H. Elgemeie, H.A. Elfahham, S.A.S. Ghozlan and M.H. Elnagdi, Bull. Chem. Soc. Jpn., 1984, 57, 1650.
6. J. Elguero, A. Fruchier, L. Pappalardo and M.C. Pardo, An. Quím., 1978, 74, 1529 and references therein.
7. M. Begtrup, R.M. Claramunt and J. Elguero, J. Chem. Soc. Perkin Trans. II, 1978, 99.
8. G. Tóth, A. Szöllösy, A. Almásy, B. Podányi, I. Hermeicz, T. Breining and Z. Mészáros, Org. Magn. Reson., 1983, 21, 687.
9. J.B. Stothers, 'Carbon-13 NMR Spectroscopy', Academic Press, New York, 1972, p. 282.

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