

Benzotriazol-1-yl-acetone as a Building Block in Heterocyclic Chemistry: a Route to Benzotriazolypyridazines, Benzotriazolylphthalazines and Benzotriazolypyrazolo[5,1-*c*]-1,2,4-triazines

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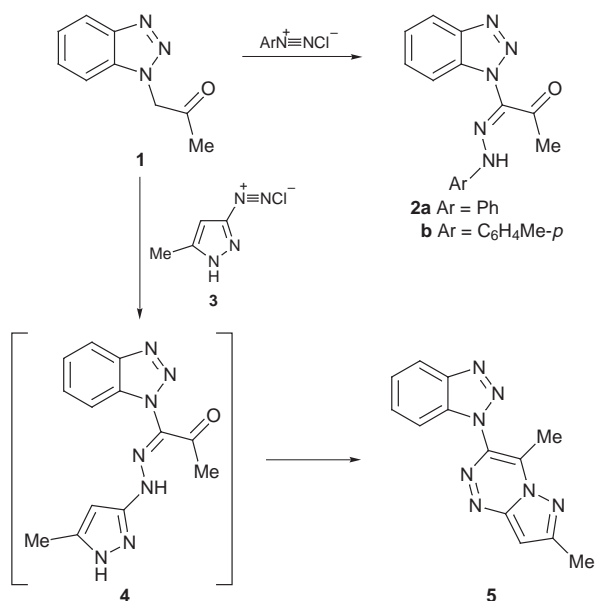
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J. Chem. Research (S),
1999, 648–649
J. Chem. Research (M),
1999, 2801–2810

Benzotriazolylacetone is coupled with aromatic diazonium salts to yield arylhydrazones, which can be condensed with ethyl cyanoacetate yielding pyridazinones whose reactivity towards activated double bond systems is investigated.

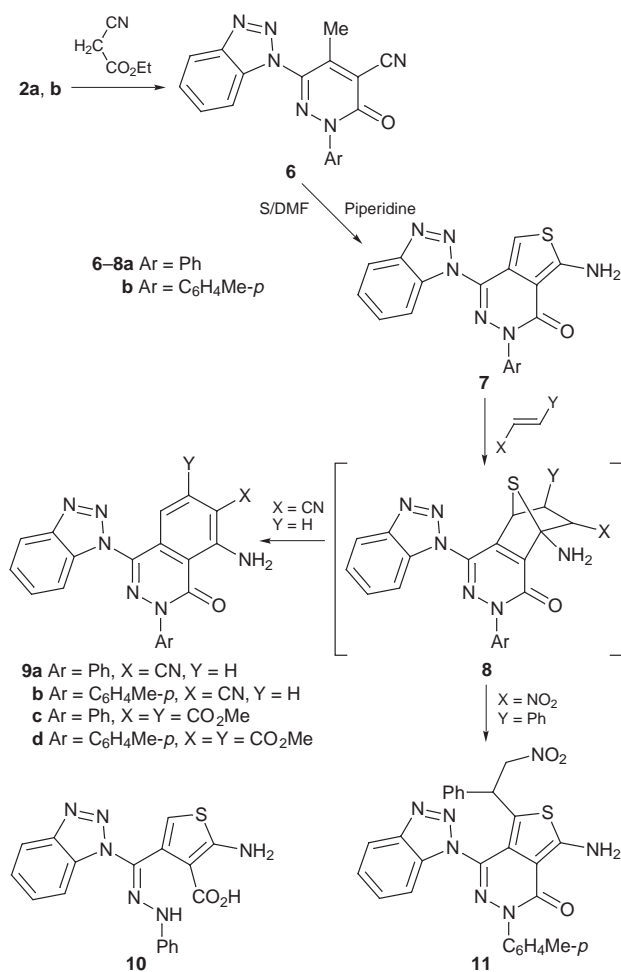
In conjunction with our interest in the synthesis of azines and condensed azines^{3,4} we investigated the reactivity of benzotriazolylacetone **1** toward aromatic and heteroaromatic diazonium salts as a route to new azines and condensed azines of potential activity as agrochemicals. Thus, compound **1** coupled smoothly with aromatic diazonium salts in ethanolic sodium acetate to yield the corresponding arylhydrazones **2a,b** in good yields (Scheme 1). On the other hand, coupling of **1** with diazotized 5-methyl-1*H*-pyrazolamine **3** resulted in the formation of the pyrazolo[5,1-*c*]-1,2,4-triazole derivative **5**, which is formed, most likely, *via* intermediacy of the pyrazolohydrazone **4** (Scheme 1).



Scheme 1

Compounds **2a,b** condensed with ethyl cyanoacetate to yield the pyridazinones **6a,b** in excellent yields (Scheme 2). These pyridazinones reacted with sulfur in dimethylformamide and in the presence of piperidine to yield the thienopyridazin-6-ones **7a,b** in good yields (Scheme 2). Compounds **7a,b** reacted with acrylonitrile and with dimethyl acetylenedicarboxylate to yield the

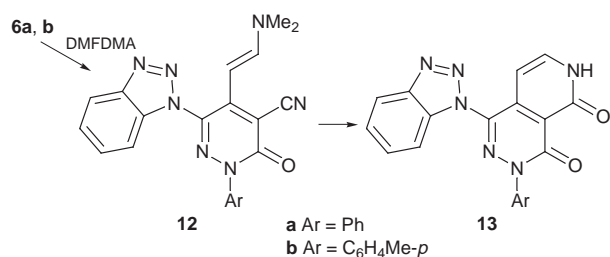
phthalazines **9a,d**, believed to be formed *via* the intermediacy of cycloadducts **8a-d** (Scheme 2). On the other hand attempted reaction of **7a** with diethyl fumarate or ethyl propionate in aqueous acetic acid, afforded only the carboxylic acid derivatives **10** (Scheme 2). This is in contrast to the reported addition of diethyl fumarate and ethyl propionate to thienoazines and thienocoumarins.^{3,4}



Scheme 2

The reaction of **7b** with ω -nitrostyrene afforded a 1:1 adduct. Initially it was thought that this product was cycloadduct **8**; X = NO₂, Y = Ph. However, this structure

*To receive any correspondence.

**Scheme 3**

was not in accord with its observed chemistry and spectra. Thus, the reaction products were fairly stable on reflux in acetic acid–hydrochloric acid which would be expected to effect ready ring opening of the thiabicycloheptene moiety. Moreover, ¹³CNMR spectroscopy indicated the presence of only two sp³ carbons while **8** should show four such carbons. Possible addition at the amino function was also readily excluded as both IR and ¹HNMR spectroscopy revealed the presence of the amino function. Structure **11** which is in accord with spectral data was thus suggested (Scheme 2). Although traces of C-1 alkylation products have been isolated earlier as side products from the reaction of electron-poor acetylenes with

thienopyridines,⁵ only recently have high yield C-1 alkylation reactions of thienopyridazinones with electron-poor olefins been observed.⁶ These products are believed to be formed *via* rearrangement of the formed cycloadducts.

Compounds **6a,b** also condensed with *N,N*-dimethylformamide dimethyl acetal to yield the enaminones **12a,b** (Scheme 3). These were cyclized into **13a,b** on reflux in acetic acid–hydrochloric acid.

Techniques used: IR, ¹H and ¹³CNMR, elemental analysis

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Received, 13th July 1999; Accepted, 4th August 1999
Paper E/9/05641F

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