Routes to a New Triazolyl System—Substituted 3-Amino-4,5-diaryl-triazoles

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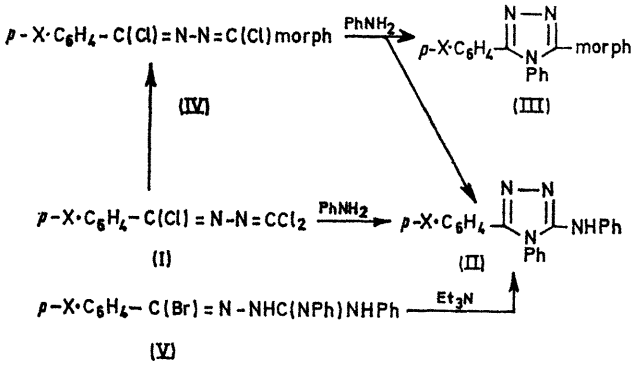
Summary 4-(*p*-Substituted phenyl)-1,1,4-trichlorodiazabutadienes (I) react with aniline to yield the new 3-amino-4,5-diaryl-triazoles (II), which are also obtained by the 1,3-dipolar reaction of 1-bromomethyleneamino-2,3-diphenylguanidines with triethylamine.

WE report the formation of new 3,4,5-trisubstituted triazoles (II) in high yields from 4-(*p*-substituted phenyl)-1,1,4-trihalogeno-diazabutadienes (I)[1,2]. When aniline (1·5 ml) is added to compounds (I) (1 g) at room temperature a spontaneous, vigorous, exothermic reaction takes place with the formation of gums. These on treatment with hydrochloric acid (0·025N; 30 ml) and water (30 ml) yield the triazoles (II) (analysis and molecular weights): X = NO_2, m.p. 250° (90%); X = Br, m.p. 237—239° (92%); X = Cl, m.p. 240—242° (95%); X = Pr^i, m.p. 200—202°, (94%).



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morph = morpholine

The trichloro-compound (I) on treatment with morpholine gave a 4-(*p*-substituted phenyl)-1,4-dichloro-1-morpholino-diazabutadienes (IV).[1] These when treated with aniline at room temperature also gave gums which when treated, as above, with hydrochloric acid and water gave crystalline mixtures which were further separated by extraction [benzene, ether, or light petroleum (b.p. 40—60°)]. The benzene-insoluble materials were the triazoles (II) and those soluble in benzene were the triazoles (III). The combined yield of both triazoles was greater than 93% in all cases. The structures of compound (III) were also established by analysis and molecular weight determinations and their yields and m.p. are as follows: X = NO_2, m.p. 183—184°, (23%); X = Br, m.p. 193—195°, (20%); X = Cl, m.p. 190—192°, (19%); X = Pr^i, m.p. = 170—172°, (4%).

If the methine-carbon–halogen bond in compounds (I) is the last to be substituted then 1-halogenomethyleneamino-2,3-diphenylguanidines (V) should be intermediates in the conversion of the diazabutadienes (I) into the triazoles (II). Proof of this was obtained by first preparing the novel 1-bromo-(*p*-substituted phenyl)methyleneamino-2,3-diphenylguanidines (V). When a suspension of these in triethylamine was stirred, compounds (II) were obtained in high yields.

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[1] F. L. Scott, J. Donovan, and J. K. O'Halloran, *Tetrahedron Letters*, 1970, 4079.
[2] F. L. Scott and J. K. O'Halloran, *Tetrahedron Letters*, 1970, 4083.