Crown Ether Catalysed Synthesis and Cycloaddition Reactions of Arenediazocyanides

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Summary Arenediazocyanides, prepared from arenediazonium tetrafluoroborates by a crown ether catalysed phase transfer reaction, undergo a variety of reactions including the Diels–Alder cycloaddition with numerous dienes.

AFTER many years of misinformation,[1] the reaction of arenediazonium compounds with dienes was shown to yield reduced pyridazines or pyridazinium salts[2] rather than open-chained dienes. In retrospect, it does not seem remarkable that arenediazonium cations undergo cycloaddition since many N=N-containing species undergo such reactions, so a positively charged species should do so even more readily.[3] Nevertheless, the cycloaddition of arenediazonium cations in polar, organic solvents has not proved to be a general method for the synthesis of *N*-arylpyridazines. Attempted cycloaddition reactions of arenediazonium ions made soluble in non-polar media by crown ether complexation have been similarly unsuccessful.[4] The cyanide derivatives of arenediazonium salts (arenediazocyanides) were not at first considered useful in this respect because classical methods for their synthesis have generally afforded poor yields.[5] Further, no general dienophilic reactivity has been reported for aromatic azo compounds.[6] We report here a general synthesis of arenediazocyanides, and several interesting reactions of these compounds, including the high-yield [2 + 4]-cycloaddition to a variety of dienes.

Arenediazocyanides may be prepared by stirring stable arenediazonium tetrafluoroborates[7] with solid KCN (1 equiv.) and 18-crown-6 (0·05 equiv.) in CH_2Cl_2 for several hours at ambient temperature. In the absence of crown ether low yields of arenediazocyanides are obtained even after 120 h. Quaternary ammonium salts are not useful phase-transfer catalysts[8] for this reaction, for reasons other than diazonium salt solubilization,[9] and this will be discussed elsewhere. By this method,† the following compounds were prepared: (**1**), 95% yield, m.p. 29 °C (previously reported as an oil[10]); (**2**), 87—91%, m.p.

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† The yield given is for material isolated directly from the reaction mixture and having ^{1}H-n.m.r. and i.r.-spectral properties consistent with the assigned structures and identical to those properties observed for analytically pure material. The m.p. in parentheses is either that reported in the literature or recorded for the purest sample attainable.

TABLE. Cycloaddition reactions of arenediazocyanides

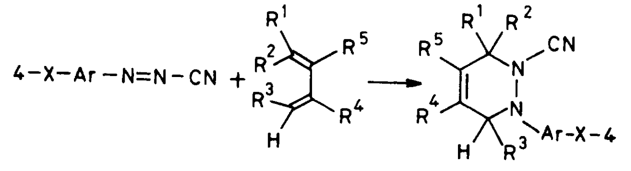
Diene	X	R^1	R^2	R^3	R^4	R^5	Isomer ratio[a]	% Yield[b]
(**7**)	Cl	H	$-CH_2-$		H	H	—	58
(**7**)	NO_2	H	$-CH_2-$		H	H	—	100
(**8**)	Cl	H	$-CH_2CH_2-$		H	H	—	43
(**9**)	Cl	H	H	H	H	H	—	85
(**10**)	OMe	Me	H	H	H	H	8:1	47
(**10**)	Cl	Me	H	H	H	H	4:1	100
(**10**)	NO_2	Me	H	H	H	H	2:1	96
(**11**)	Cl	H	H	H	Me	H	10:1[c]	55
(**12**)	OMe	H	H	H	Me	Me	—	70
(**12**)	Cl	H	H	H	Me	Me	—	90
(**12**)	NO_2	H	H	H	Me	Me	—	94

[a] The isomer given is the major isomer. Isomer ratios and structures were assigned by detailed ^{1}H- and ^{13}C-n.m.r. analysis. [b] All cycloadducts are new compounds and gave satisfactory nitrogen combustion analyses as well as the expected ^{1}H- and ^{13}C-n.m.r. spectra. [c] Estimated from ^{13}C-n.m.r. data.

117—122 °C (121—122 °C);[11] (**3**), 92%, m.p. 60—61 °C;‡ (**4**), 75—91%, m.p. 100—104 °C (105°);[11] (**5**), 78—84%, m.p. 124—128 °C (132 °C);[11] and (**6**), 80—91%, m.p. 82—85 °C (86 °C).[12] The crude products exhibited ^{1}H-n.m.r. and i.r. spectral properties indistinguishable from analytically pure material which may be obtained by vacuum sublimation, distillation, or crystallization.

The arenediazocyanides may be hydrolysed readily by HCl–tetrahydrofuran at ambient temperature to yield Ar–N=N–CO–NH_2. When (**4**) was heated with NaOD in D_2O, 4-chlorodeuteriobenzene (28%) was obtained and identified by gas chromatographic–mass spectroscopic analysis, indicating that loss of CO_2 and N_2 probably occurs from Ar–N=N–CO_2^- to form an aryl anion which is then protonated.[13] When (**4**) is heated (90 °C) with $PdCl_2$ and NaOAc in HOAc for 6 h, a 60% yield of 4,4′-dichlorobiphenyl is isolated. The generality and mechanism of the latter reaction are not yet clear. To our knowledge, the only similar reaction to have been reported is a zerovalent palladium catalysed arylation of certain alkenes,[14] which may be unrelated mechanistically to the present work.

The cycloaddition reactions of several arylazocyanides with cyclopentadiene (**7**), cyclohexadiene (**8**), butadiene (**9**), *E*-piperylene (**10**), isoprene (**11**), and 2,3-dimethylbutadiene (**12**) which occur according to equation (1) are summarized in the Table.



(**1**) X = H
(**2**) X = MeO
(**3**) X = F
(**4**) X = Cl
(**5**) X = Br
(**6**) X = O_2N

(**7**)—(**12**)

The cycloaddition reaction appears to be a simple [2 + 4] process of the Diels–Alder type. The reaction between (**4**) and excess of (**12**) was followed by ^{1}H-n.m.r. spectroscopy at 26, 37, and 45 °C. The rate constants at these temperatures were found to be $1{\cdot}08 \times 10^{-4}$, $2{\cdot}92 \times 10^{-4}$, and $5{\cdot}04 \times 10^{-4}$ l mol^{-1} s^{-1}, respectively, and the activation energy and entropy were found to be 15·5 kcal mol^{-1} and −26·9 cal mol^{-1} K^{-1}, respectively (1 cal = 4·184 J).

Not only do the arylazocyanides undergo smooth cycloaddition reactions with a variety of dienes, but 4–Cl–C_6H_4–N=N–CO–NH_2,[15] the partially hydrolysed derivative of (**4**) also proved to be a reactive dienophile.

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‡ A satisfactory combustion analysis was not obtained for this compound: calc. for $C_7H_4N_3F$: C, 56·4; H, 2·7; N, 28·2. Found: C, 55·3; H, 2·4; N, 27·35%. Spectral properties, especially the expected F–H and F–C n.m.r. couplings were in agreement with the assigned structure.

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